UNIVERSIDADE DE LISBOA
FACULDADE DE CIÊNCIAS
QUÍMICA E BIOQUÍMICA

Test and Development of Microcapsules for Rigid Polyurethane Foam

Mestrado em Química Tecnológica

Dissertação Pública

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Acknowledgement:

This thesis presents the work developed in a nine-month internship at Greenseal Research Ltd. Its elaboration had the crucial support, dedication and patience of several people.

To begin, I want to thank to Prof. Maria José Lourenço for all the support regarding scientific knowledge and for providing me the opportunity to contact with Greenseal Research.

I would like to thank Dr. Aster De Schrijver for the opportunity to develop my work at Greenseal Research, and to all his team, in special Dra. Ana Clara Marques, who supervised my work and provided me all the support I needed during this internship. Also, I would like to thank Prof. João Bordado, for the scientific knowledge and all his team for the laboratorial support provided.

To my family and friends, Ana Rita Antunes, Inês Sebastião, Cláudia Oliveira, Mónica Araújo and Andreia Sofia, I would like to thank all the support, patient and encouragement during this important step in my life.

Finally, I would like to thank to José Rodrigues for being my listener, for giving me his time and support and for being there when I needed the most.

Abstract

The main purpose of this work was to produce microcapsules, with an encapsulated curing agent, to incorporate in one component polyurethane foams, in order to accelerate the foam curing process.

During this work, inorganic silica based microcapsules and also those organically modified (hybrid composition) were produced, by an approach that combines the micro-emulsion technique with the sol-gel method. Varied newly developed shell compositions have been screened and assessed. In particular, the addition of silicones and cork powder to the synthesis was studied, in an attempt to combine and achieve desired properties. Also, several reactional parameters were studied, in order to optimize the microencapsulation process and microcapsule features, reduce the synthesis costs and increase the reaction yield. In a final part of this work, a "pre-scale-up" of a previous selected synthesis was made.

All the microcapsules were subjected to physical and chemical characterization technics. Scanning electron microscope, SEM, analysis was used to characterize the microcapsules regarding their morphology, size and agglomeration. The Fourier transform infrared spectroscopy, FTIR, characterization was useful to understand the molecular structure of the shell, in order to confirm the presence of certain reactional groups. The FTIR technique has also enabled to compare, between different syntheses, the amount of glycerol that was encapsulated, however the thermogravimetric analysis, TGA, characterization was fundamental to have a precise notion of its amount. The other characterization techniques employed in this work had been previously developed at Greenseal Research and were aimed at studying the leaching of the encapsulated compound, as well as evaluating the effect of the microcapsules on the OCF foams.

The hybrid (organically modified) microcapsules did not have a perfect spherical shape and most of them were agglomerated. Nevertheless, they exhibited a lower leaching, when comparing with inorganic silica based ones, and, in some cases, the amount of encapsulated glycerol was almost the same.

Finally, the silica based microcapsules with a second shell of amino-functional silica were found to be the best choice to apply in polyurethane foams, since the microcapsules had a perfect spherical shape, were not very aggregated, were poly-nucleated, did not exhibit significant leaching and led to a significant increase in the curing rate.

Key Words: Microcapsules; Sol-Gel; Polyurethane Foams; Hybrid-microcapsules; Curing; TEOS;

Resumo

O mercado dos poliuretanos encontra-se, de momento, em expansão. No ano de 2012, a Asia foi o maior produtor de poliuretano, tendo sido responsável pela produção de cerca de 10 milhões de toneladas, seguida pela Europa com uma produção anual de 4 milhões de toneladas. No ano de 2013 a produção mundial de latas de espuma de poliuretano atingiu as 600 mil toneladas, sendo esperado que em 2018 a sua produção a nível mundial atinja as 820 mil toneladas [1].

No que diz respeito às espumas de poliuretano de um componente, o mercado tem apresentado um crescimento anual, sendo mais notório em mercados emergentes. No ano de 2013 foram produzidas mundialmente 535 milhões de latas e estima-se que em 2018 sejam produzidas cerca de 668 milhões de latas [1].

As espumas de poliuretano de um componente têm tido uma utilização crescente na indústria de construção civil, por exemplo na fixação e vedação em portas e janelas, preenchimento de buracos, isolamento em edifícios, etc. Ao contrário das espumas de poliuretano de dois componentes, em que os polióis e os isocianatos não são armazenados em conjunto, no caso de espumas de poliuretano de um componente, estes encontram-se misturados e reagidos numa lata pressurizada, juntamente com os gases propulsores. À mistura, no interior de uma lata pressurizada, composta pelos polióis e o isocianato é dado o nome de quasi-pré-polímero, sendo que o processo de cura será apenas completo após a dispensa (“spray”) da espuma, quando ocorre contacto com a humidade do ar, formando-se uma espuma de poliuretano-poliureia rígida. Deste modo, a velocidade de cura deste tipo de espuma encontra-se fortemente dependente da humidade do meio em que foi feito o spray, levando a que seja mais lenta que no caso das espumas de poliuretano de dois componentes.

O estágio que me foi proporcionado pela empresa Greenseal Research, teve como principal objetivo o desenvolvimento de microcápsulas à base de sílica, inorgânicas e organicamente modificadas (híbridas), contendo um composto encapsulado, com o intuito de serem aplicadas em espumas de poliuretano de um componente, numa tentativa de aumentar a velocidade do seu processo de cura. O composto a encapsular, glicerol, contém grupos O-H que vão contribuir para o processo de cura.

Durante o processo de spray do poliuretano, as microcápsulas deverão ser quebradas mecanicamente, devido à diferença de pressão a que se encontram no interior da lata e a pressão a que são sujeitas no exterior. Após a quebra das microcápsulas, o composto encapsulado é libertado, entrando em contacto com o pré-polímero e, em conjunto com a humidade do meio ambiente, contribuir para o processo de cura da espuma, acelerando-o.

Foram sintetizadas e caracterizadas diversas microcápsulas ao longo deste trabalho. Para a sua síntese foi utilizada a técnica sol-gel, combinada com a tecnologia das emulsões. Esta técnica baseia-se na polimerização de um percursor (alcóxido), previamente hidrolisado, em torno das gotículas das micro-emulsões, que contém o composto a encapsular. Observou-se que a polimerização ocorre do exterior para o interior da gotícula, levando à formação de uma cápsula que contem no seu interior o composto desejado. Através desta técnica foi possível sintetizar tanto microcápsulas inorgânicas, a partir do percursor tetraetilortossilicato, TEOS, como microcápsulas híbridas, utilizando para isso os percursores metil-trietoxisilano (MTES) e (3-glicidiloxi-propil)trimetoxi-silano (GPTMS), com funcionalidade orgânica metil e glicidilóxi, respetivamente, em conjunto com o tetraetilortosilicato. Foram também sintetizadas microcápsulas de sílica com uma dupla parede utilizando, em adição ao tetraetilortossilicato, um aminosilano. Para além das sínteses referidas, foram ainda sintetizadas microcápsulas às quais se adicionaram outros constituintes, como silicones e pó de cortiça, na tentativa de estas adquirirem algumas características dos compostos adicionados, obtendo-se as propriedades desejadas. Foram ainda feitos estudos de vários parâmetros reacionais, como a possibilidade de adição de dois tensioactivos, um em cada fase da emulsão (dispersa e contínua), a adição de um catalisador, a quantidade de tensioactivo a adicionar, entre outros, numa tentativa de conseguir otimizar o processo de encapsulação e as características das cápsulas, diminuir os custos de produção das mesmas e ainda tentar aumentar o rendimento da reação.

Na fase de incorporação das microcápsulas nas latas de espuma foi necessário ter em atenção alguns aspetos, de modo a garantir que a qualidade e tempo de vida do material dentro da lata não diminuíssem com a adição das microcápsulas. Foi assim

necessário garantir que as microcápsulas não se encontrassem agregadas, nem apresentarem grandes dimensões, o que poderia levar à ocorrência de acumulação das mesmas com consequente obstrução do "nozzle" logo após o primeiro "spray", impossibilitando uma posterior utilização da lata. Foi ainda necessário garantir que o composto encapsulado não estava a ser libertado do interior das cápsulas, o que, caso acontecesse, levaria à cura antecipada do pré-polímero ainda dentro da lata, inviabilizando o produto. A libertação do glicerol prévia ao "spray", pode ocorrer quer por saída do mesmo através dos poros da cápsula, quer por quebra das microcápsulas no interior da lata.

Durante o estágio foram utilizadas diversas técnicas de caracterização químicas e físicas. A técnica "microscopia electrónica de varrimento", permitiu caracterizar as microcápsulas ao nível morfológico, ou seja se estas são mononucleadas, polinucleadas ou se do tipo matriz porosa, perceber se existe e qual o nível de aglomeração das microcápsulas e ainda ter uma noção da sua dimensão e da sua gama de tamanhos. A técnica de espectroscopia de infravermelho por transformada de Fourier permitiu a deteção de grupos químicos específicos nas microcápsulas, o que possibilitou confirmar a existência de determinados compostos e assim a ocorrência de algumas reações químicas durante a síntese. Esta técnica foi ainda importante pois permitiu ter uma noção da quantidade do composto encapsulado, por comparação da banda correspondente aos grupos O-H e das restantes bandas relativas ao glicerol, entre espectros de diferentes sínteses. No entanto a análise termogravimétrica foi fundamental para obter uma noção quantitativa do glicerol encapsulado. Foram ainda feitos alguns testes, previamente desenvolvidos na Greenseal Research, que permitiram perceber se as microcápsulas apresentavam lixiviação e ainda qual a contribuição das mesmas para o processo de cura das espumas.

As microcápsulas de sílica apresentam uma forma esférica perfeita, pouca aglomeração e são as cápsulas que apresentam maior quantidade de glicerol encapsulado, no entanto são de grandes dimensões e apresentam um grau de lixiviação não aceitável para a aplicação, levando a uma diminuição significativa do tempo de vida da lata. Comparativamente, as microcápsulas que foram obtidas com os percursores metil-trietoxisilano e (3-glicidiloxi-propil)trimetoxi-silano não apresentam

uma forma esférica perfeita e encontram-se mais aglomeradas, no entanto, no geral, apresentam tamanhos mais pequenos e foi observada menos lixiviação. Ainda, em alguns casos, as microcápsulas híbridas aparentam conter uma quantidade de glicerol idêntica à observada nas microcápsulas de sílica. Finalmente, as microcápsulas de sílica com uma dupla parede de amino-sílica apresentam-se como uma boa opção para a aplicação em espumas de poliuretano, uma vez que são poli-nucleadas, apresentam uma forma esférica perfeita, baixa aglomeração, reduzida lixiviação e promovem uma significativa aceleração da cura das espumas. No entanto foi observado que a utilização de um "nozzle" durante o spray, contribui para uma maior quebra das microcápsulas e consequente libertação do composto encapsulado, uma vez que, especialmente as microcápsulas mais pequenas, têm dificuldade em ser quebradas pela diferença de pressão.

Na fase final do estágio foi realizado um estudo prévio ao "scale-up", i.e. a quantidade de reagentes foi aumentada para o dobro, da síntese de microcápsulas de sílica com uma segunda parede de amino-silica. Após diversas tentativas, é possível considerar que o "scale-up" foi bem conseguido, tendo sido obtidas microcápsulas idênticas às da síntese prévia ao "scale-up" e um aumento da quantidade de microcápsulas obtidas para aproximadamente o dobro. Com a utilização de um "nozzle" durante o processo de "spray", foi observada uma diminuição no tempo de cura da espuma de cerca de 30 minutos com a aplicação das microcápsulas, por comparação com a espuma de referência, o que corresponde a uma diminuição de 44% no tempo necessário para a cura da espuma.

Como estudos futuros, poder-se-ia tentar obter microcápsulas de sílica com uma dupla parede de amino-silica, do tipo "core-shell", numa tentativa de conseguir encapsular maior quantidade de glicerol, ao mesmo tempo que se mantém a resistência mecânica típica destas cápsulas. Ainda, poderia ser interessante, tentar encapsular um catalisador, em conjunto com o glicerol, de modo a tornar a aceleração do processo de cura, das espumas contendo microcápsulas, ainda mais significativa.

Palavras-chave: Microcápsulas, Sol-Gel, espumas de poliuretano, microcápsulas híbridas, cura, TEOS

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Glossary of abbreviations

DEG – Diethylene Glycol

DME- Dimethyl Ether

EDA – Ethylenediamine

FTIR – Fourier Transform Infrared Spectroscopy

GPTMS - Glycidoxypropyl Trimethoxysilane

HLB- Hydrophilic-Lipophilic Balance

LPG- Liquefied Petroleum Gas. In this work, it is considered to be a mixture of isobutane and propane of known proportions

MTES- Methyltriethoxysilane

OCF- One Component Foam

TEOS- Tetraethyl Orthosilicate

TGA- Thermogravimetric Analysis

1. Scope and Objectives

The one component polyurethane foams, OCF, market has been showing an annual growth, mainly taking place in emerging markets. The OCF foams have also been increasingly used by professionals in the construction industry, for example, in doors and window frames, to seal gaps, to insulate buildings, among others applications.

The internship at Greenseal Research, to conclude the master's degree in Technological Chemistry at Faculdade de Ciências of Universidade de Lisboa, had as main goal the development of hybrid microcapsules, using the sol-gel technique, to encapsulate a curing agent, for the application in OCF rigid foams, with the purpose of accelerating the foam curing process. The OCF foams cure is dependent of the room humidity, which makes this process much slower in comparison with two components polyurethane foams. The present work has an ultimate goal of finding a new reliable way to decrease this difference, by accelerating the foam curing process and making it independent of the environment moisture. This will lead to an increase of the OCF performance and, therefore, enlarging the range of potential applications.

The microcapsules developed must fulfil the following requirements:

- Ensure that microcapsules will not diminish the quality of the foams:
    - Lifetime of the (quasi) pre-polymer inside the can; which can be affected by the occurrence of leaching of the encapsulated material and by the breakage of the microcapsules before spraying;

    - Obstruction of the spraying nozzle; if the microcapsules size is too big, after one spray, there can be accumulation of microcapsules in the spraying nozzle, making the can unusable.

- Control the release of the encapsulated compound:
    - If the microcapsules break before spraying, the pre-polymer will cure inside the can, making it unusable;

    - If the microcapsules do not break after spray, the encapsulated compound will not be released and will not contribute to the foam curing process.

2. Greenseal Research

To accomplish my master's degree, an opportunity to work as an internee at Greenseal Research Ltd. was provided.

Greenseal Chem is a Belgium chemical company, which main goal is to respond to the demands of OCF formulators for specialty chemicals raw materials, having into account the production of green and sustainable foams.

Greenseal Chemicals Research Center located in Lisbon, where the internship took place, is specialized in the production and development of raw materials and formulations for OFC as well as in the development of microcapsules, with an encapsulated curing agent, to added to OCF, which is expectable to lead to fast and self-curing foams.

In Fig. 1 a scheme is represented with the R&D areas in which Greenseal Chemicals Research Center is committed. During my internship I worked as a research technician in the microencapsulation investigation department of Greenseal Research, helping to achieve the desired microcapsules to add to the OCF formulation.

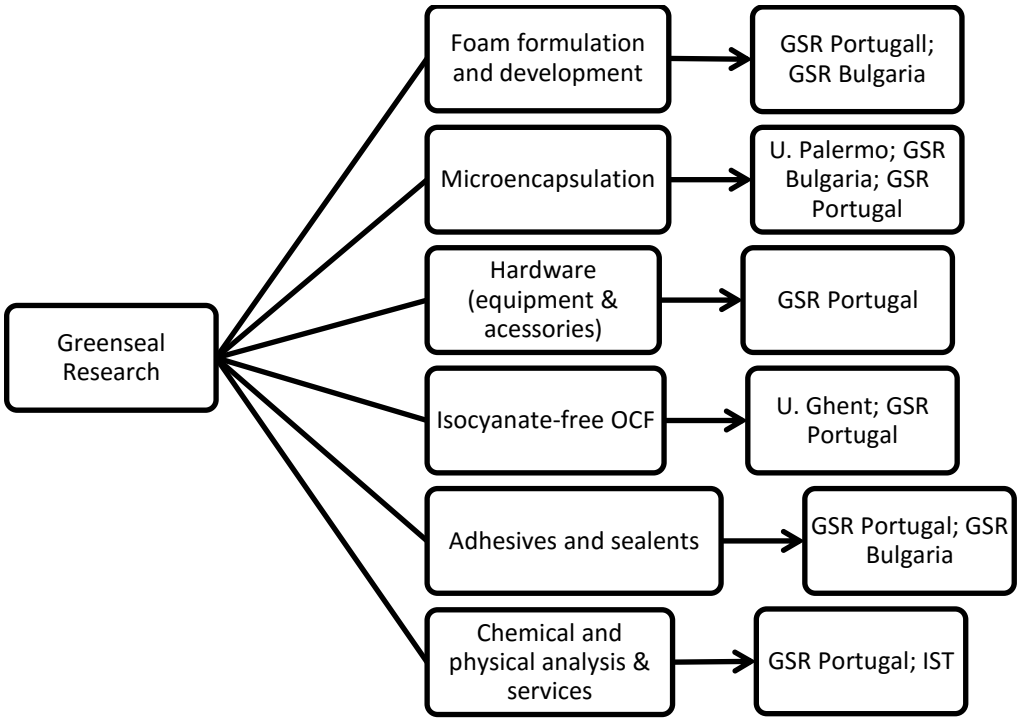


Fig. 1 – Schematic representation of the Greenseal Research R&D areas

3. Introduction

3.1. Polyurethane

3.1.1. Polyurethane History

The beginnings of the plastic industry is dated back to 1868, with the synthesis of cellulose nitrate [2]. But it was only after the early 1900's, that the most used synthetic polymers of our days began to appear: with one of the first being the polyvinyl chloride (PVC) in 1930, followed by polyethylene and polyvinylidene chloride, both in 1933, polyamides in 1934 and polytetrafluoroethylene (Teflon) in 1938 [3].

It was in 1849 that Wurtz and Hoffmann found the urethane linkage, essential for the appearance of polyurethane, by studying the reaction between an isocyanate and a compound with an alcohol functional group [4]. However it was only in 1937 that Otto Bayer and the research team he led at I.G. Farben AG chemical company discovered the polyurethane chemistry [3][5]. It was also in this year that these compounds began to be industrially produced, and the first patent associated with polyurethanes was also filled. Later, numerous other patents related to polyurethanes were filed [2][3][4].

The commercial development of polyurethanes began in Germany in the late 1930's with production of rigid polyurethane foams, adhesives and inks, while elastomers only began to be produced in 1940, in Germany and England [5]. During the Second World War, there was some development in the polyurethane science, however it was only after 1946 that the polyurethane market showed a big increase [5]. The commercial development of flexible polyurethane foams occurred in the 1950's decade, but it was only in the 1970's that semi-flexible foams and semi-rigid foams began to be used, coated with thermoplastic materials, in automobile industry [5]. It was also in that decade, that one component polyurethane foams (OCF) was developed, by the chemical group Imperial Chemical Industries, however, several years passed before OCF was used. Sweden was the first country to use these foams, but it was in Germany that OCF was fully developed and became successful [6].

3.1.2. Polyurethane's chemistry

There is more than one criteria to classify polyurethanes. They can be classified regarding their method of application, typological classification or shape of the polymer, as represented in Fig. 2

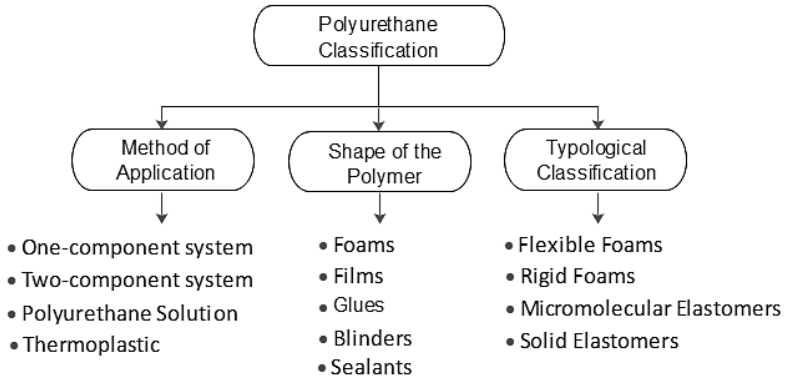


Fig. 2 - Polyurethane classifications criteria.[4]

The four principal types of polyurethane products are elastomers, foams, fibers and coatings. However the major application of this polymer is as rigid or flexible foams [2].

Polyurethane is a polymer characterized by having urethane interunit linkages in its chain, represented in Fig. 3, but not necessary in a regular order. The formation of this group occurs by the reaction of an isocyanate group with a hydroxyl group (R-OH), however isocyanates can also react with compounds with free hydrogens, like water, primary and secondary amines, carboxylic acids, amides, and others, leading to the formation of other chemical groups [2][4][7][8], such as urea, ester, amine, ether, etc. that can also be present in the polymer molecule [3][4][7][8].

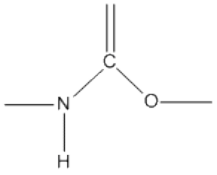


Fig. 3 - Urethane group

The most common process for polyurethane production involves the reaction between a di or polyisocyanate, and a compound with two or more alcohol groups, for example polyester polyol or polyether polyol, represented in Fig. 4 [2][4][7][8]. Typically, the reaction medium has the following constituents: polyol; catalyst, expansion agent, surfactant, polyisocyanate and other specific additives.

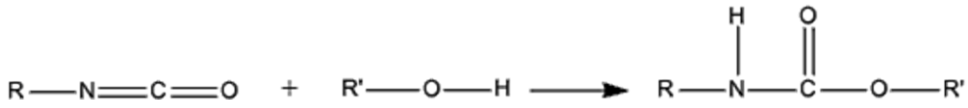


Fig. 4 - Reaction between an isocyanate and an alcohol, forming an urethane group

For the production of a tridimensional polyurethane structure it is necessary that at least one of the reagents, involved in the reaction, represented in Fig. 4, have three or more functional groups, otherwise the product obtained will be a straight polyurethane chain [4]. There are other secondary reactions that also contribute for the reticulation of the polymer, for example the reaction of an isocyanate with an urethane group, which leads to the production of allophanate, and the reaction of an isocyanate with an urea group, which leads to the production of a biuret species, as well as the reaction of dimerization and trimerization of the isocyanates. These reactions take place under certain reactional conditions of temperature or in the presence of a catalyst [4], and are responsible for the increase of the pre-polymer viscosity inside the can.

The reactions described above lead to the increase of the reactional medium temperature as well as of the viscosity of the liquid, leading to the formation of a macroscopic solid. Furthermore, in the case of the production of polyurethane foams or micromolecular elastomers, the process of expansion is also fundamental to obtain the final product [4].

3.1.3. Polyurethane foams

Polyurethane foams can be divided into rigid foams, flexible foams and micromolecular foams. In the Table 1 are presented some final applications [4][8].

Table 1 – Final applications for polyurethane foams [4][7][8]

Final applications		
Rigid polyurethane foams	**Flexible foams**	**Micromolecular foams**
Thermal insulation of buildings and refrigerators	Automotive seating	Soles
Packaging	Textile laminates	Application in joints
Buoyancy aids in boats and flotation equipment	Cushioning for diverse industrial applications	Insoles

Flexible polyurethane foams are obtained from low functional polyols with high molecular weight. This leads to the formation of a low number of crosslinking and, consequently, a flexible molecular structure. In order to obtain rigid polyurethane foams, high functional polyols with low molecular weight are used, since a great level of crosslinking is desired [4].

As referred above, in 3.1.2, for the production of polyurethane foams, as well for the production of micromolecular elastomers, the final expansion, during the synthesis, is fundamental to obtain the desired product. Essentially, the expansion results from the formation of gas in the reactional medium, leading to the increase of the global volume. The expansion stops when the pressure inside the cells equals the resistant tension of the walls of the foam cells [4]. The gas used in the expansion process can be derived from a chemical or a physical process. In the case of a chemical process, the gas is formed from the reaction between an isocyanate group and water, with the formation of urea. In the case of a physical process, the gas is formed from the vaporization of a low ebullition liquid that is added to the reactional medium [4].

3.1.3.1. One component polyurethane foams (OCF)

In one component polyurethane foams, OCF, the polyols and the isocyanates are mixed and reacted together in an aerosol can or pressure vessel, and stored along with the propellants, producing a mixture called (quasi) pre-polymer, with isocyanate in excess [9][10]. Contrariwise, in the case of two components polyurethane foams, the two components, isocyanate and polyols, are not mixed together until the application of the foam [6].

In OCF, the three referred components are mixed together in the aerosol can or pressure vessel, with all the polyols reacting with the isocyanate groups, so that the OCF product mixture, the polyurethane (quasi) pre-polymer, remains with an excess of isocyanate groups and, therefore, remains liquid. The completion of the curing process of the fresh foam takes place after spraying, between the isocyanate groups (in excess) and the humidity in the environment. Being so, the velocity of the curing process is dependent of the humidity of the local where it is applied [6][9][10].

In more detail, the OCF chemical process involves four stages. In the first stage, polyol, isocyanates and propellants are added to the aerosol can or pressure vessel. In this stage, the pre-polymer is formed, with formation of urethane bonds. After spraying, because of the fast evaporation of the propellants, the pre-polymer rapidly expands into a low-density froth. The fresh foam, in contact with air, reacts with the ambient humidity, resulting in conversion of the remaining –NCO groups of the isocyanate, into amino groups with production of CO_2. The CO_2 produced in this stage will lead to a second expansion of the foam and heat release. The sprayed foam will thus expand and produce a fully cured foam of polyurethane-polyurea composition [9][11].

3.1.3.2. Polyurethane production and consumption

The polyurethane market is currently a growing market. It was estimated that, the global polyurethane market revenue was worth 35,89 billion euros in the year of 2012, and is expected to reach 55,40 billion euros by 2018 [12].

In the year of 2012, Asia was the major global polyurethane producer, with about 10million tons of polyurethane produced, followed by Europe, with about 4 million tons[13]. In the following year, 2013, the major producer of polyurethane foams was China, with 35% of the global production, followed by America with 41% [1]. In that year the total global production of polyurethane sprays foam was about 600 thousand tons and nowadays this value is still growing, being estimated to reach 820 thousand tons by 2018 [1].

Regarding OCF, in that same year, 2013, the global production was about 534.5 million cans and it is estimated that by 2018 the number of cans produced will reach 667.7 million cans [1]. In this year, the world larger producer of OCF cans, with 34% of the global production was also China, which can be seen in Fig. 5. However, EMEA, i.e. Europe, the Middle East and Africa region group, still represents the largest region in terms of OCF production, with 55% of the total global production, as shown in Fig. 5. From the EMEA region, most of the production is centered in Eastern Europe, with Estonia and Poland being the largest producers [1].

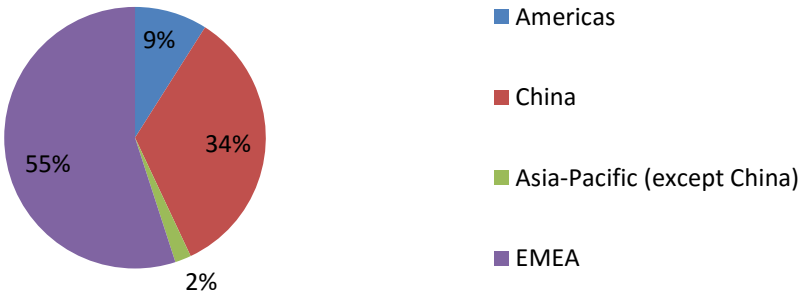


Fig. 5 – Global production of one component foam by region, 2013 [1]

- China was the major global producer of polyurethane in 2012, as well as the major polyurethane foam producer, and specifically OCF, in 2013;
- From the EMEA group, Eastern Europe, with Estonia and Poland had the major OCF production, in 2013.

In the year of 2012, polyurethane was the commodity polymer not characterized by a simple structure that had a larger consumption, with 6% of the global plastic

consumption, as can be seen in Fig. 6, 22% of the total of the polyurethane produced this year, 22% was rigid polyurethane foams, with the higher value registered for production corresponding to 28% of all the polyurethane production. In this year, China and the U.S. together share 35,9% of the total polyurethane foam consumed [13][12].

In the year of 2011, in Europe, the polyurethane demand reached 7% of the total plastic request, as it can be seen in Fig. 7, and in comparison with the year 2010, the demand of this polymer showed a significant growth, mainly for uses in construction and isolation [14]. Regarding OCF, in the year 2013, Europe was considered the most knowledgeable and demanding market of the EMEA region [8].

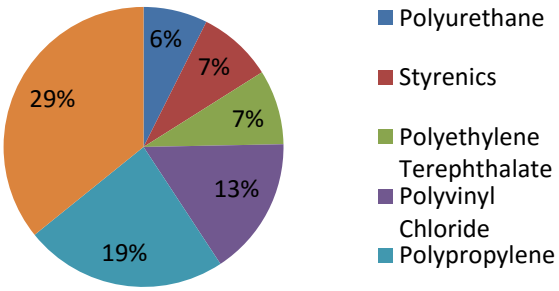


Fig. 6- Percentage of global consumption of plastics in 2012. Polyethylene includes all densities; styrenics includes all copolymers along with atactic polystyrene [3].

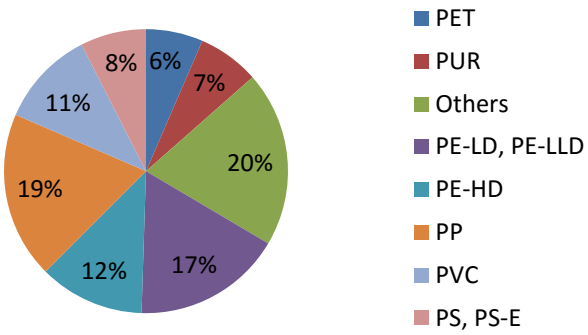


Fig. 7 – European plastics demand, 2011. Source: Plastics Europe Market Research Group (PEMRG) [14]

- In 2012, 6% of the global plastic consumption was polyurethane;
- 22% of the total polyurethane produced in 2012, 22% was rigid polyurethane foams;
- In 2011, in Europe, the polyurethane demand reached 7% of the total plastic request.

3.2. Microcapsules and microencapsulation

3.2.1. Microencapsulation

Microencapsulation can be described as the process of enclosing micron-sized particles of solids or droplets of liquids or gases, inside a second material, using an inert encapsulating agent, providing them protection and isolation from the external environment. The capsules are characterized as microcapsules when their diameter is between 1 and 1000 µm [15][16][17]. The inert surrounding material will be referred, in this work, as “shell”.

Encapsulation of different compounds is an evolving area in chemistry with a significant importance in many industrial sectors, such as pharmaceutical, agrochemical, food, textile and cosmetic industries [18][19][20]. Microcapsules are used to ensure that the encapsulated compound reaches the desired area of action without being affected by the environment, for example by acting as a carrier system, by protecting the encapsulated materials from detrimental conditions and separating the encapsulated material from incompatible components. Microcapsules are also used to control the rate and the moment in which the encapsulated compound is released, for example delaying the external chemical reactions and controlling the moment of capsule rupture and the release profile of the encapsulated agent [21][22].

Microcapsules may have spherical or irregular shape, and can be divided into two distinct parts, the core and the shell. While the core contains the active ingredient and is the intrinsic part of the microcapsule, the shell protects the core material from the external atmosphere and corresponds to the extrinsic part of the microcapsule [23].

The release of the encapsulated material can occur for example by rupture, outside pressure, by melting, drying, dissolution in solvent or by degradation of the shell [23].

Microcapsules can be classified through their size or morphology [22]. Regarding their morphology, microcapsules can be divided in three categories: porous matrix, mononuclear, and polynuclear microcapsules, as represented in Fig. 8 (a), (b) and (c) respectively [24]. In the case of matrix type microcapsules, the core is integrated homogeneously within the matrix of the shell material, while mononuclear type microcapsules, or core-shell, have a single hollow core surrounded by a shell. Lastly, polynuclear type microcapsules are characterized by having a number of different sized cores enclosed within the shell. Beside these three basic morphologies, microcapsules can also form clusters or be mononuclear with multiple shells [22][23] .

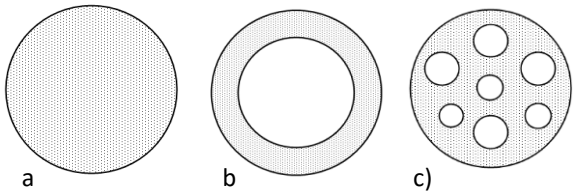


Fig. 8 – Schematic representation of the diferent microcapsules morphology, a) matrix microcapsule b) mononuclear microcapsule c) poly-nuclear micarocapsule (Adapted from [24]**)**

There are several encapsulation technics and, in general, they are divided into two basic groups, chemical and physical, with the latter being subdivided into physic-chemical and physic-mechanical technics, as schematically represented in Fig. 9[23].

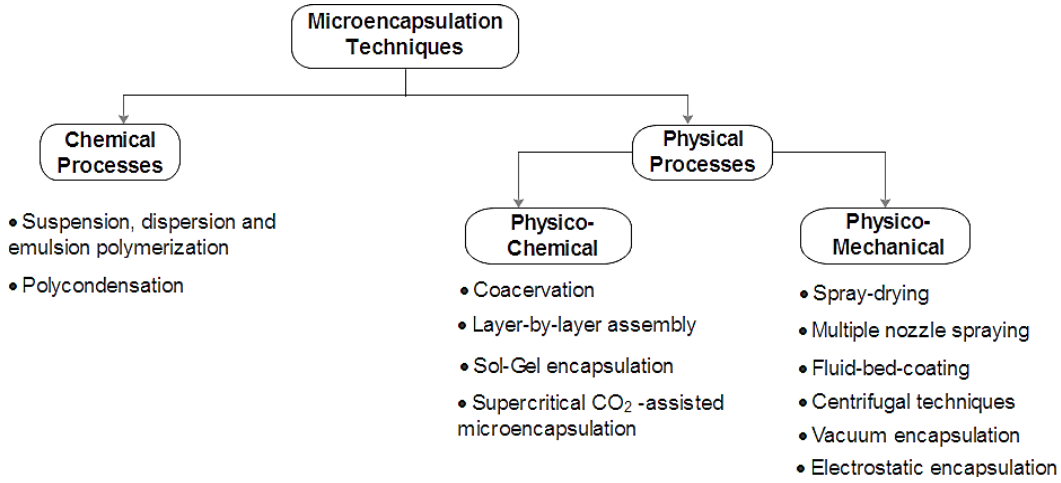


Fig. 9 – Different techniques used for microencapsulation[23]

3.2.1.1. Release of the encapsulated compounds

Microencapsulation is an ideal method to achieve a desired delay of the release of the active compound; therefore one of the most important characteristic of microcapsules is the control of the release profile [23].

The release of the encapsulated compound can be achieved by two different processes: controlled release or targeted release [16][22][23]. In the case of controlled release, the encapsulated molecules are slowly released. This type of release is desired when long-term effects are required. In the case of targeted release, the encapsulated substances are released at once, for example, when the shell material is dissolved or pressure is applied to the capsule [23].

There are several mechanisms in which microcapsules can release their content at appropriate time. For the release to happen, it is necessary a stimulus, for example a mechanical, chemical or a thermal stimulus [23]. The most common mechanisms in which the encapsulated compounds are released is by mechanical rupture, dissolution or melting of the microcapsule. However, there are other release mechanisms, although less common, like ablation or biodegradation [22].

The control of the final microcapsule characteristics, such as pore size, shell thickness and permeability of the shell, is of major importance for the control of the release profile. For example, in case of release by breakage of the shell, by a mechanical rupture, as schematically represented in Fig. 10 an optimal combination of shell thickness is necessary; if the shell wall is too thick the microcapsule will not be easy to rupture, however if the shell is too thin, it might be too fragile [25]. In case of release by degradation of the shell, for example by dissolution as in represented in Fig. 10, the release of the encapsulated compound is delayed until certain environmental conditions occur, for example a chemical stimulus. In this case, the rate of the release can be tailored by controlling the thickness of the shell as well as the composition, its solubility in the dissolution fluid [23]. As for a final example the fracture of the shell upon swelling of the core, also represented in Fig. 10. In this case, the shell must act as a semi permeable membrane, since it has to allow the creation of an osmotic pressure difference between the inside and the outside of the microcapsule, which will lead to drive the encapsulated compound out of the capsule, through its small pores. In this case, the control of the permeability of the shell is of great importance, since it must allow the diffusion of the solvent into the core [17][23].

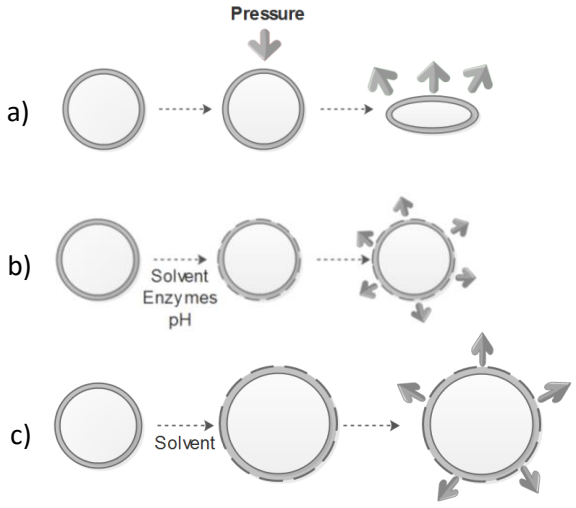


Fig. 10 – Schematic representation of some release mechanisms. a) Example of release by breakage of the shell, by mechanical rupture. b) Example of release by breakage of the shell, by dissolution. c) Example of release by fracture of the shell, by swelling. (Adapted from [23]**)**

3.2.1.2. Silica- based microcapsules

Historically, organic compounds such as synthetic polymers, have been used more often than inorganic compounds as the encapsulating material, however polymer-based microcapsules normally suffer from poor chemical and physical stability [18][26]. Until 2008, very few inorganic, silica-based, controlled-release microcapsules have been industrially produced, due to relative difficulty in manipulating the internal structure of the particles and the high processing temperature employed, which makes the synthesis process unviable [16].

Recently, studies have been made to optimize the synthesis of silica-based capsules. The increased interest in inorganic microcapsules is due to their distinguishing characteristics, like robustness, thermal and mechanical stability, chemical resistance, non-toxic quality for the environment, biocompatibility, and the ability to easily incorporate additional functional groups [16][18][20][21].

Sol-gel technology emulsion method, an abbreviation for “solution-gelling”, has shown to be the most effective and economical method for the synthesis of hollow silica microspheres. This technic allows the synthesis of inorganic structures without lacking the control of the microstructure of the particles and the need of high processing temperatures, thus offering a cost-saving process [16][20][23]. With this method it is possible to control the micro or nanostructure of the particle, pore size, shape, capsule size and density of the particle, through thoughtful choice of the parameters of the reaction [20][27].

3.2.1.3. Hybrid microcapsules

Organic– inorganic hybrid microparticles, which have been called “organically modified silica” (“Ormosil”), are of great interest because of the potential of combining properties of organic and inorganic components. Organic compounds offer structural flexibility and inorganic materials provide stability, robustness and chemical resistance [28].

Using the sol-gel technique, Ormosil compounds are easy to obtain, just like inorganic microparticles. They can be obtained with the same approach using organically-modified silicon alkoxides as co-precursors [29]. Furthermore, Ormosil compounds also have the advantage, enabled by the sol-gel process, to control the shape, density, and surface properties, such as in case of the inorganic materials [24].

3.2.2. Sol-gel microencapsulation process

3.2.2.1. Sol-gel process

Sol-gel science has been rediscovered during the second half of the twentieth century and, since then, it has led to a great number of applications and spin-offs. This technique has shown to be an important synthesis method in several domains of research, such as in optics, electronics, biomaterials, and semi- and superconductors, mainly because of the diversity of the materials obtained, versatility and low cost compared to other techniques [23].

In a brief manner, the sol-gel technique can be divided into the following reactional steps: hydrolysis; condensation; gelation; aging; and drying [20][27].

It is also important to refer that this technique is usually combined with emulsion technology, in order to result in a microencapsulation process [20]. The emulsion droplets are said to act as a micro-reactors; when an active compound is located inside an emulsion droplet, encapsulation will occur as the pre-hydrolyzed precursors polymerize to build a cage around the active compound, at the interface between the dispersed and continuous phase [16].

As the name suggests, the process begins with the preparation of a “sol”, which leads to a posterior formation of a “gel”. A “sol” is defined as a colloidal suspension of solid particles in a liquid. Colloids are suspensions of particles, with linear dimensions between 10nm and 1μm, with particle interactions dominated by short range forces such *Van der Waals* attractions or hydrogen bonding [23][30]. The precursors to

prepare a colloid, consist of a metal or metalloid element surrounded by ligands, not consisting of another metal or metalloid atom. The class of precursors most widely used for sol-gel technique is alkoxides, a member of the family of the metalorganic compounds. Metal alkoxides have the general formula $M(OR)_{z,}$ where M is the metal ion, R is an alkyl group and z is the valence state of the metal and they are most commonly used because they react readily with water, facilitating the hydrolysis reactional step. The alkoxide most thoroughly studied example is tetraethyl orthosilicate, TEOS, $Si(OC_2H_5)_{4,}$ represented in Fig.11 [23][30].

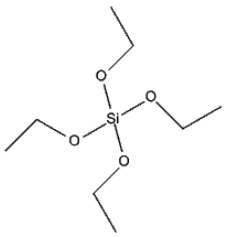


Fig.11- Representation of a tetraethyl orthosilicate molecule

3.2.2.2. Emulsion technology

An emulsion can be defined as an heterogeneous system containing two immiscible phases composed by at least two liquids, one in the form of a droplet dispersed into the other [20]. Emulsions are typically obtained through mixing of the two components and are, usually, in the presence of an emulsifier, so that a stable emulsion is produced [31][32]. In the particular case of microemulsions, they are composed by two immiscible liquids, with particles of diameter ranging, approximately from 1 to 100 nm, usually 10 to 50 nm, according to IUPAC definition [31][33].

Typically, emulsions are composed by an aqueous liquid phase and a hydrocarbon phase, or so called oil phase. Given this, there can be four types of emulsions; W/O emulsions, in the case of water droplets dispersed in oil and O/W emulsions, for oil droplets dispersed in water, as represented in Fig. 12, and double emulsions; combinations like W/O/W and O/W/O emulsion. For example, O/W/O emulsions are the abbreviation for oil droplets dispersed in aqueous droplets that are, in turn

dispersed, in a continuous oil phase, as can be seen in Fig. 13 [18][32][34]. Emulsions can also be O/O, oil in oil, when two oils have different polarities [33].

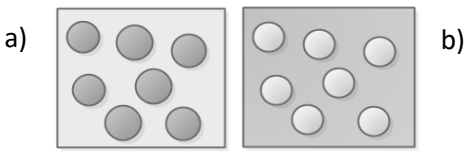


Fig. 12- a) Oil in water emulsion b) (O/W) b) Water in oil emulsion (W/O)

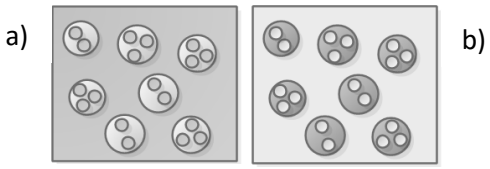


Fig. 13- a) Oil in water in oil emulsion (O/W/O) b) water in oil in water emulsion (W/O/W)

For sol-gel encapsulation technique, the type of emulsion chosen is dependent on the solubility of the molecules to be encapsulated [18]. As for water soluble molecules, they can be directly encapsulated in a W/O emulsion. In this case, the molecule is located in the aqueous droplet, which is dispersed in the nonpolar solvent. By the contrary, if the molecules to be encapsulated are not water soluble, an O/W emulsion is used, with the compound located in the oil phase [20].

3.2.2.2.1. Surfactant

Surfactants are molecules with an amphipathic (or amphiphilic) structure; this means the molecule has both a hydrophilic and a hydrophobic group. Usually, the hydrophobic group consists of a long hydrocarbon chain, while the hydrophilic group is composed by an ionic or highly polar group. On an emulsion system, the hydrophobic portion of the surfactant molecules orient themselves with the hydrophobic phase, i.e. the oil phase, while the hydrophilic portion orients toward the hydrophilic phase, i.e. water, as schematically represented in Fig. 14 [33].

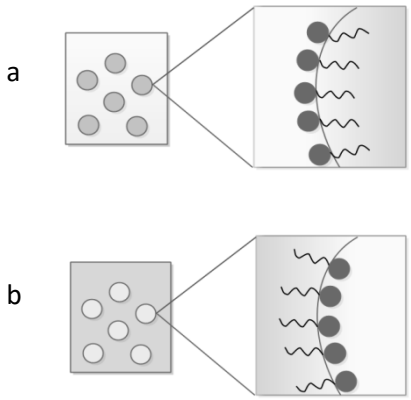


Fig. 14 – Schematic representation of the distribution of a surfactant in the interface of an emulsion. a) O/W emulsion b) W/O emulsion

Depending on the nature of hydrophilic group, surfactants can be classified as: anionic; cationic; zwitterionic; and nonionic [31]. The presence of a surfactant helps to stabilize the emulsion, and the solvent-surfactant combination as well as the nature of the surfactant, helps to control the droplet size distribution and the emulsion viscosity [16][20][34][35]. For the sol-gel encapsulation technique, it is of great importance to control the size and stability of the emulsion droplet, since it acts as a nano-reactor and therefore influences the size of the final particles [16].

The word surfactant is a contraction of the term “surface-active agent” and, as the name suggests, it is a substance that act on the surface or interfaces. An interface can be described as a boundary between two immiscible phases, whereas a surface is an interface where one phase is a gas and the other liquid. A surfactant, when added at low concentration to a system, has the capability to be absorbed by some or all the surfaces or interfaces in the system and change their free energy. The interfacial free energy is described as the minimum amount of work required to create the interface. It can be used to determine the interfacial tension between two phases, since it is a measure of the interfacial free energy per unit area, as seen in (Equation 1). The interfacial/surface tension is also a measure of the difference between the two phases intersection at the interface/surface. A bigger dissimilarity between their nature leads to higher value of the surface or interfacial/surface tension [31][33][34].

A surfactant, by lowering the interface free energy, leads to a lower superficial tension and, consequently, to a decrease in the pressure difference across the drop interface, as seen in (Equation 2) [33].

$$\Delta G = \gamma \times \cup \Delta A$$ **(Equation 1)** [36]

Where ΔG is the interface/surface free energy, Nm/J; ΔA is the total interfacial area of the disperse phase, m^2; ɣ is the interfacial tension, N/m.

$$\Delta P = \gamma \times (\frac{1}{R1} + \frac{1}{R2})$$ **(Equation 2)** [33]

For a perfectly spherical droplet, R1=R2=R and;

$$\Delta P = \frac{2\gamma}{R}$$ **(Equation 3)** [33]

Where ΔP is the pressure difference across the drop interface, ɣ is the surface tension, R1 and R2 are the principal radii o curvature and R is the radii of the droplet.

An important surfactant characteristic is the HLB, hydrophilic-lipophilic balance. The HLB of a surfactant represents the affinity of the surfactant to the water and to oil. Its value is expressed as a ratio between the hydrophilic and lipophilic groups of the amphiphilic surfactant molecule [20]. When HLB value is higher than 10, it indicates hydrophilicity of the surfactant, and when HLB value is lower than 10 it indicates lipophilicity [20]. Thus, in general, surfactants with low HLB value, between 3 and 8, are incorporated into the oil based solution. Contrariwise, surfactants with high HLB value, between 8 and 18, are incorporated into water-based solutions, due to their hydrophilic character [20][24][31][32]. However, HLB value only gives information about the emulsifying characteristics of the surfactant, not its efficiency. For example, all surfactants with high HLB value are O/W emulsifiers (if placed in the continuous phase), however not all of them have the same efficiency for a particular system. The HLB is important for the stability of the emulsion, nevertheless the chemical type of the emulsifier is important as well [32][34].

3.2.2.3. Sol-gel reaction steps

3.2.2.3.1. Hydrolysis

The hydrolysis reaction of the alkoxide precursors leads to the formation of a hydroxide specie [23]. Through the mixing of water with the alkoxide precursor, the alkoxysilane's alkoxy groups (OR) are replaced with hydroxyl groups (OH), as represented in Fig. 15. The reactional parameters that most influence the hydrolysis reaction are the pH of the reaction medium (nature of the catalyst) and the concentration of the catalyst. However, there are other secondary parameters that have also some influence in the hydrolysis; the H_2O/Si molar ratio, temperature, and solvent used [23][30].

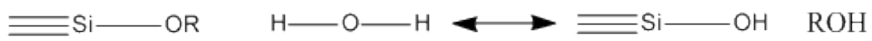


Fig. 15 – Hydrolysis of a Si alkoxide

Hydrolysis reaction can occur without the addition of a catalyst, however, it is most rapid and complete when they are employed. The catalyst for this reaction is a basic or acidic catalyst. The rate of hydrolysis reaction has a minimum at pH 7 and increases when pH gets higher or smaller than 7. However, for an equivalent catalyst concentration, acidic-catalyzed hydrolysis reaction is faster than basic catalyzed-hydrolysis [18][20][23][30].

In acidic conditions, it is likely that, in a first step, the alkoxy group of the alkoxysilane is rapidly protonated, as represented in Fig. 16. After this first step, the electron density of the silicon atom is removed, making it more electrophilic and therefore more susceptible for an attack from water, Fig. 16 [23][30].

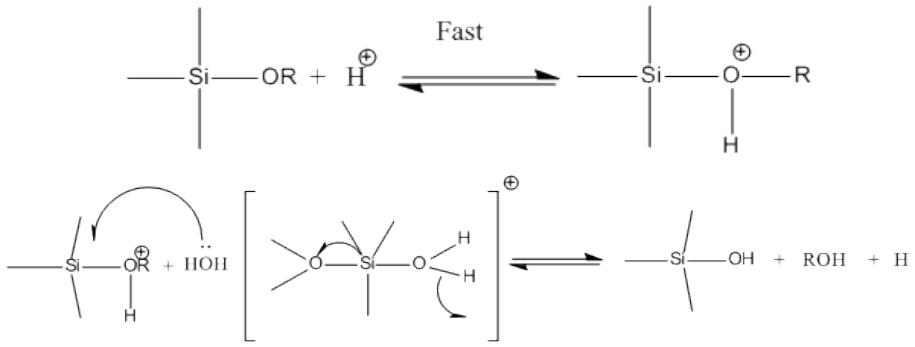


Fig. 16- Example of acid – catalyzed hydrolysis, of a Si alkoxide [23]

In basic conditions, it is likely that the hydrolysis reaction begins with a rapid first step of dissociating water to produce hydroxyl anions, which will then attack the silicon atom, represented in Fig. 17 [23]. Basic hydrolysis, is a much slower process than acidic-hydrolysis, because basic alkoxide oxygens tend to repel the nucleophilic –OH. Nevertheless, after an initial hydrolysis reaction occurs, the following reactions proceed stepwise with each subsequent extraction of an alkoxide group easier than the previous one [23].

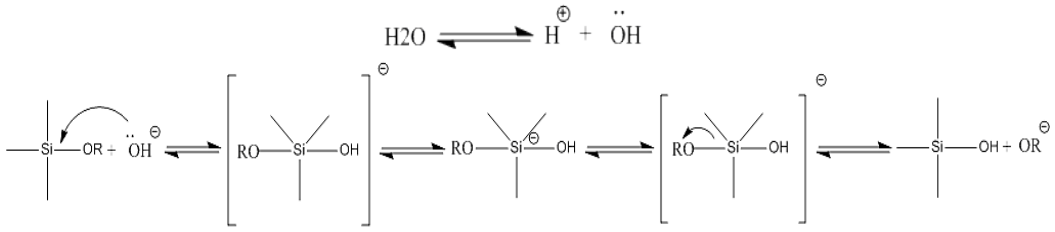


Fig. 17- Example of basic – catalyzed hydrolysis of a Si alkoxide [23]

3.2.2.3.2. Condensation

Through following condensation reaction, oxide species are formed. This reaction involving the silanol groups (Si-OH) obtained in the previous hydrolysis reaction, leads to the formation of siloxane bonds (Si-O-Si), and the byproducts alcohol, if the condensation occurs via dealcoholation, or water, if via dehydration, as represented in

Fig. 18 a) and b) [20][23][30]. When preparing multi-metal-oxides, condensation can occur both as self-condensation, and M-O-M bonds are obtained, or as cross-condensation, where M-O-M' bonds are formed [23].

As the number of siloxane bonds increases, the individual molecules are bridged and aggregate in the "sol" and an inorganic oxide network is built up progressively [23]. Under most conditions, condensation reactions begin before hydrolysis is complete. Nevertheless, certain reactional conditions like pH, H_2O/Si molar ratio and catalyst can lead to a complete hydrolysis reaction, before the condensation reactions begin [23].

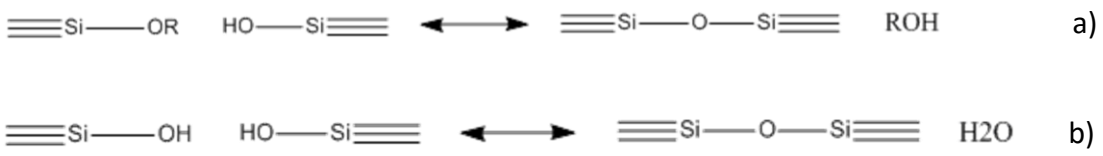


Fig. 18 – Condensation reactions of a Si alkoxide

As in hydrolysis reactions, condensation can occur without the use of a catalyst. However, their use can be helpful. The catalysis in sol-gel technique is of the same nature in either hydrolysis or condensation reactions, acting as a basic or acidic catalysis [23]. However, the rate of condensation, contrariwise to hydrolysis, shows a minimum around pH 2 and obtains a maximum at pH 7, starting to decline as pH gets higher than 7 [18][20][30].

3.2.2.4. Gelation and aging

Gelation can be defined as the changes in properties that occur as a sol, when transforming into a gel [30]. In a simple way, clusters are formed by hydrolysis and condensation reactions, until they collide; at this point links are formed between the clusters to produce a single one called a gel. While the gel forms, there will be many clusters present in the sol phase, which will progressively become connected to the

network and increase the stiffness of the gel, until the last link is formed and a spanning cluster is created [30].

The next step of a sol-gel reaction is the aging process and it can be defined as the mechanism in which changes in structure and properties occur. Through this stage, there is the formation of further crosslinks, with covalent links replacing the nonbonded contacts. The network becomes stronger, stiffer and shrinks. Structural evolution with changings in pore sizes and pore wall strengths also occur [23][30].

3.2.2.4.1. Drying

Lastly, the product must be dried, in order to lose the remaining water, alcohol and other volatile components [23]. In case of porous materials, the process of drying encompasses several stages. It begins with liquid evaporation, which causes shrinkage of the body, which corresponds to the volume of the liquid lost. In this stage, the liquid-vapor interface is at the surface of the body. When it becomes too stiff to shrink, the liquid recedes to the interior, which leads to air filling the pores at the surface. Nevertheless, a continuous liquid film supports the flow to the exterior and evaporation continues at the surface. In a last stage, drying can only occur by evaporation of the liquid within the body, while the vapor diffuses to the outside [30].

3.2.2.5. Catalysis

The catalysis in the sol-gel technique is achieved using a basic or acid catalyst. The pH at which the synthesis takes place dictates the type of silica particle produced, since it has influence in the porosity, size and homogeneity of the final particle, as seen Fig. 19 [18][20][23]. The catalysts more widely used in sol-gel technology are mineral acids or ammonia, but acetic acid, potassium hydroxide (KOH), amines, potassium fluoride (KF), hydrofluoric acid (HF), titanium alkoxides, and vanadium alkoxides and oxides are also generally used [30].

In the case of an acid-catalyzed reaction, the hydrolysis step has the higher rate of velocity, being the condensation the rate-limiting step. Consequently, a small growth is observed and small particles are formed, with loose and open structure [20][24]. Contrariwise, when the sol-gel process is catalyzed by a basic catalyst, the condensation reaction of the pre-hydrolyzed silanes has the higher rate of velocity, and the reaction of hydrolysis is hindered at some extent. The rapid condensation of the hydrolyzed precursors leads to the production of large and dense particles, with essentially no porosity [23][24]. The Sol-Gel synthesis can also be done through a "two-step" approach. In this method, the hydrolysis takes place under strong acidic conditions, followed by condensation catalyzed by a base. The resulting material is large mesoporous microspheres [24].

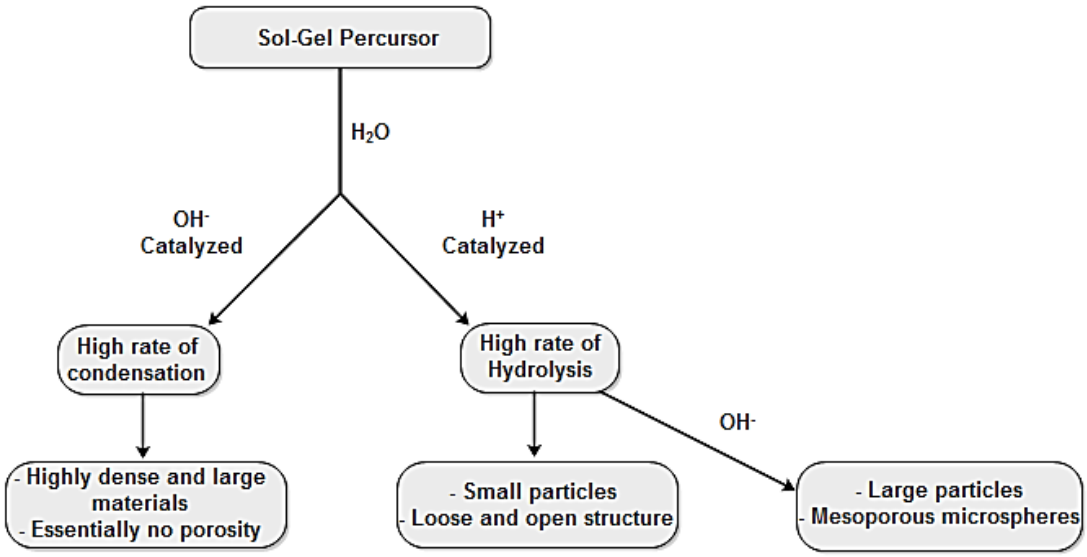


Fig. 19 – Sematic representation of the effect of a catalyst in hydrolysis, condensation and final particle characteristics

4. Experimental Part

4.1. Testing and characterization

In this chapter, the tests and characterizations used during the internship, for the microcapsules evaluation, will be explained. Some physical characterizations and tests were made including: optical microscope observation, scanning electron microscopy (SEM), leaching tests in Ongronat® 2500, which is an oligomeric MDI, and tests to evaluate the effect of the microcapsules in OCF foams. Regarding the chemical characterization, the techniques used were Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA).

4.1.1. Physical testing and characterization

4.1.1.1. Optical microscope

The observation under optical microscope was the characterization technique used right after the synthesis. It allowed a first perspective of the obtained microcapsules, regarding its morphology type, i.e. porous matrix, core-shell or poly-nucleated, dimensions and aggregation.
The microscope used was a Kruss, MSZ 5600optical microscope.

4.1.1.2. Scanning Electron Microscopy

Scanning electron microscopy (SEM) was used to complement the evaluation obtained from the optical microscope. The SEM analysis provided information regarding the topographical features, morphology, size distribution and agglomeration.

Previously to this analysis, the microcapsules were subjected to heating for 24 hours at 45°C in order to remove possible remaining water. The microcapsules were fixed to a

carbon conductive tape and glued in a sample holder. Lastly, the sample was coated with gold.

The SEM analysis was made using a JEOL JSM7001F with a FEG (field emission gun) microscope.

4.1.1.3. Leaching test

The leaching test was made with the purpose of understanding if the encapsulated glycerol was leaching out from the microcapsules without their breakage, i.e. through their porosity. It is important to understand the microcapsules leaching behavior, since it can compromise the OFC can's life span.

In this test, the microcapsules were mixed with Ongronat® 2500 and its viscosity was measured over several days. The Ongronat®2500 was used in this test since it has isocyanate groups that react with the glycerol's OH groups and residual water, leading to an increase of its viscosity and, thus, enabling the detection of the leaching phenomenon, as well as OH contamination of the outer surface of the capsules. The solution used for this test was composed of 5%, in weight, of microcapsules and 95% of Ongronat® 2500.

For the leaching test, a multi speed digital cone and plate viscometer with variable temperature control from REL was used. For the analysis, a small sample of the Ongronat®2500 was collected, and placed in the viscometer. The amount of sample must be enough to cover the area where the pendulum touches. The analysis started with the limit of 20cP, however if the viscosity of the Ongronat® 2500 was too close to this value, it should be increased to a next limit.

Greenseal Research has defined a maximum viscosity value acceptable for this test. If the Ongronat® 2500 viscosity reached 5000cP, the microcapsules of such formulation were not acceptable to be used in the OFC cans.

4.1.1.4. Testing microcapsules in OCF

The following tests were made with the purpose of understanding the effect of the microcapsules in the OCF foams's curing process.

For performing these tests, an OCF aerosol can must be previously filled with the component B, an isocyanate-based pre-polymer, component A, composed mainly of polyols, the microcapsules to be tested, in a selected amount, and finally the propellant gases, as explained below, according to a proprietary formulation previously developed by Greenseal Research.

- **Can preparation**

The method presented in this work for the OCF cans preparation was previously developed by Greenseal Research.

An OCF can is composed by the microcapsules and three components: Component A, composed by a mixture of polyols, catalyst, plasticizers, silicones and flame retardants; component B, an isocyanate-based pre-polymer; and component C, the liquefied gases, liquefied petroleum gas (LPG) and dimethyl ether (DME). The microcapsules must be subjected to drying at 100ºC before being added to the can, in order to eliminate some possible water contamination at their surface. The amount of microcapsules added to the formulation was 6,8% of component A + B in weight.

The protocol method starts with the preparation of the component A, followed by its mechanical stirring for one hour. Then, the aerosol can starts to be filled with component B, followed by the microcapsules and lastly the component A is added. The amount of component A and B is such that the ratio NCO/OH is equal to 3,5. The can is then sealed with an aerosol valve. Then, LPG and DME (component C) gases, previously measured in the burettes, are forced to enter into the can. Finally, the can must be vigorously shaken.

4.1.1.4.1. String, tack free and cutting time test

One day after preparing the can, containing the microcapsules, the froth can already be sprayed onto paper substrate. Through this test, three parameters, related to the curing process of the OCF foam, are evaluated: string time, tack free time and cutting time.

The referred test was performed according to a protocol previously established by Greenseal Research, based on the OCF tests proposed by FEICA "Association of the European Adhesive & Sealant Industry", a multinational association that represents the European adhesives and sealants industry.

In this test, the OCF foam must be sprayed horizontally on paper. The string time is reached when the sprayed foam begins to be sticky and, when touching slightly on the surface with a paper, a string is formed. The tack free time is reached when the surface is no longer sticky. Lastly, the cutting time test is reached when, by cutting the foam, the cut surface is not sticky, the knife is clean, without pre-polymer residues, and the foam cells are not compressed.

In this test, a reference foam was always sprayed, i.e. a foam without microcapsules, in the same conditions as the foam containing microcapsules, so that a comparison (benchmark test) is done.

In some studies, a foam bid was also sprayed with different nozzles, which would mechanically contribute for the microcapsules' breakage.

A decrease in the string, tack-free and cutting times means an acceleration of the foam curing process.

4.1.1.4.2. Curing time test

The curing time test was made with the purpose of understanding the effect of the microcapsules in the foams' curing process. This test was performed according to a protocol previously defined by Greenseal Research.

In this test, a small bid was sprayed inside a plastic bag, which was previously purged with N_2 gas and immediately sealed, in order to avoid the entrance of air. The bag was then stored in a desiccator, in a low moisture environment. The foams were evaluated in a scale of "-5" to "5", being " -5" the evaluation given if the sprayed foam was still in liquid state and "5" if the foam was completely cured (solid). The evaluation must be followed until the foam is completely cured. In this test, a reference foam was always evaluated, i.e. without microcapsules.

In some studies, foam bids were also tested through spraying with different nozzles.

4.1.1.4.3. Shaking Rate test

The shaking rate test was made with the purpose of understanding if the microcapsules were influencing the OCF can's life span, through leaching of the encapsulated compound.

Through this test, the agitation of the pre-polymer was measured inside the can. If the microcapsules were leaching, the pre-polymer viscosity would increase and, thus, its agitation would decrease.

The shaking rate test was performed according to a protocol previously defined by Greenseal Research. It comprises the shaking of the can, for a short period, during several days after the can preparation. The agitation was evaluated in a scale from "5" to "-5", being "5" the value given to a good agitation and "-5" the value given if the material inside the can did not agitate at all.

In this test a reference can was always evaluated, i.e. without microcapsules.

4.1.2. Chemical characterization

4.1.2.1. Fourier transform infrared spectroscopy

The Fourier transform infrared spectrometry (FTIR) characterization was used in this work to confirm the presence of the encapsulated compound as well as to make a comparative evaluation of its quantity, among different syntheses. This characterization technique was also used to confirm the presence of characteristic groups, in order to verify the presence of certain compounds in the shell surface.

Before being characterized by FTIR, the microcapsules were subjected to a heat treatment at 45°C for 24h. The FTIR equipment used was a *Nicolet 5700 FT-IR* (Thermo Electron Corporation), with an ATR accessory with a diamond crystal. The transmission spectrum was obtained between 4000 and 600 cm^{-1}.

4.1.1.1. Thermogravimetric analysis

The thermogravimetric analysis (TGA), was made with the principal purpose of determining the amount of encapsulated compound in the microcapsules. This technique was used as a necessary complement to the FTIR characterization analysis, for this purpose. The TGA analyses were made in two different laboratories, in one case the TGA equipment used was a TGA 92 16-18 SETARAM, in the other one a Netzsch Luxx STA 409 PC was used. In both cases, the analyses were made in an air controlled atmosphere, at 10°C/ min

The microcapsules that were analyzed through TGA were previously subjected to a heat treatment at 45°C for 24h, in order to evaporate possible superficial water.

4.2. Presentation and discussion of results

In this chapter, the experimental procedures used during this internship, for different microcapsule's synthesis, will be described.

This chapter begins with an analysis on some reproducibility studies related to microcapsules previously synthetized in Greenseal Research, also obtained through sol-gel technique. Some studies regarding the optimization of reactional parameters for the microcapsules synthesis are described, as well as some studies regarding shell material modifications and encapsulation of different compounds. In the final part of this work, a pre- scale-up study of a previously selected synthesis is presented.

The general synthesis procedure used in this work was adopted from a previously developed protocol. During this internship, some studies were made that led to changes to this protocol. Adding to the referred studies, a new heating mantle was acquired in the final month of the internship (to improve reproducibility of the achieved product), which resulted in forced and additional process optimization activities.

The syntheses presented in this work were named according to the acronyms presented in the Table A 1, Appendix A. The given acronyms took into account the mol percentage of the silanes used in each synthesis.

In Fig. 20 a scheme of some studies is presented, regarding reactional parameters that were carried on during the internship. In Fig. 21 a scheme regarding the synthesis made during the internship is presented, which will be described in the present work.

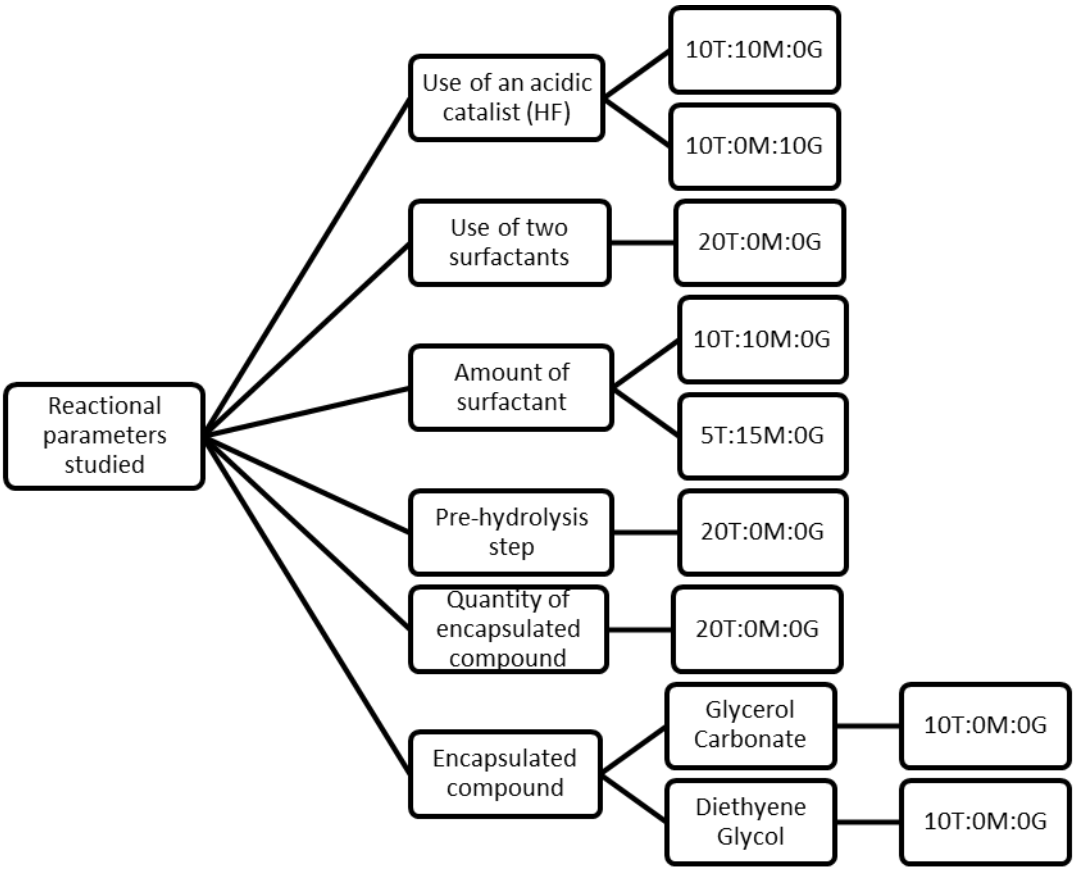


Fig. 20 - Schematic representation of the studies regarding reactional parameters described in this work

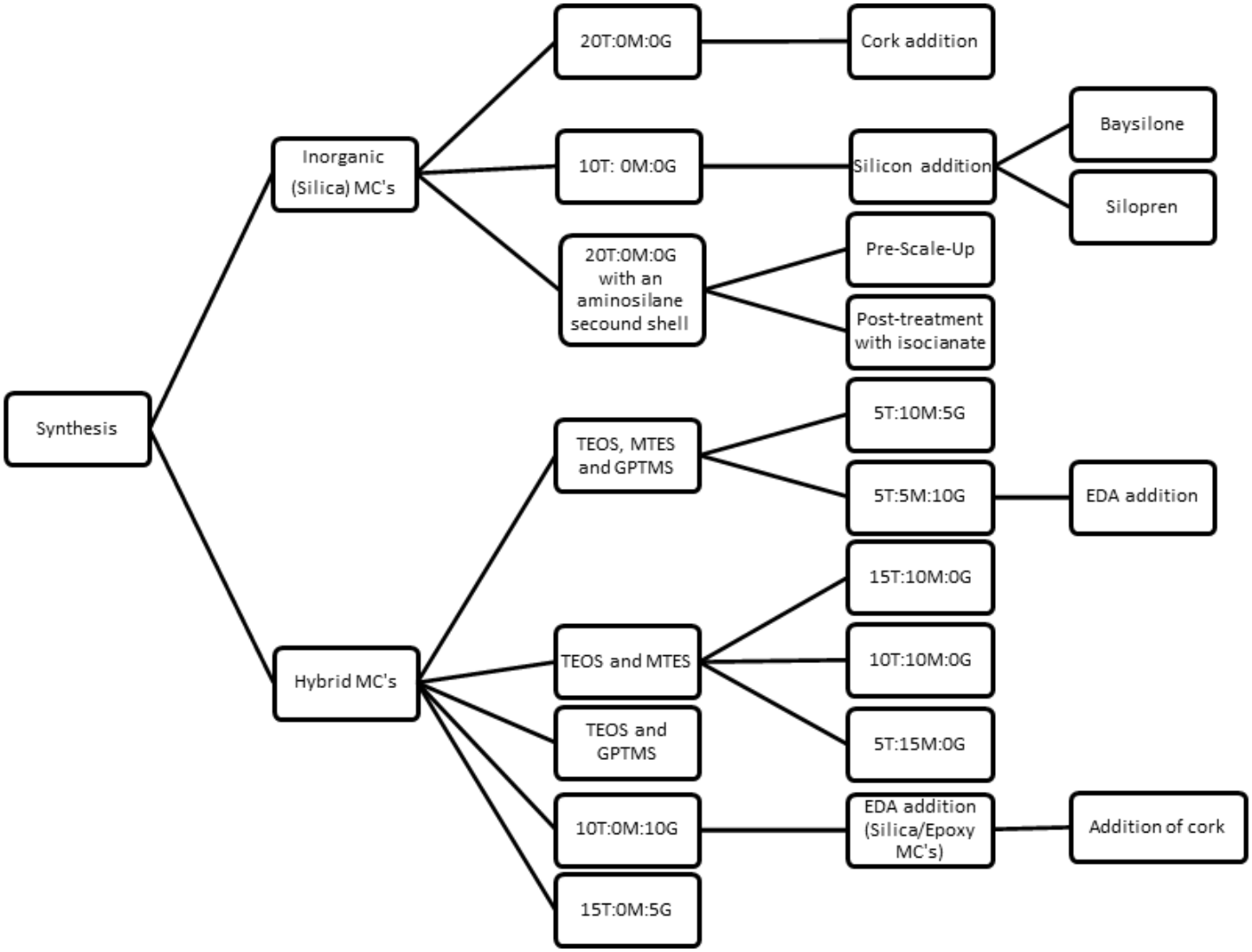


Fig. 21- Schematic representation of the synthesis described in this work

4.2.1. Synthesis of silica based microcapsules

Silica based microcapsules were synthetized following an experimental base procedure, previously developed in Greenseal Research. Throughout this work, this protocol will be referred as “experimental base procedure”. The alterations described from now on will be carried on having this protocol as a starting point.

The experimental procedure for the microcapsules’ synthesis encompassed the following steps: pre-hydrolysis of the alkoxysilanes; preparation of an emulsion solution with the encapsulating compound in the aqueous phase of the emulsion system; mixture of the emulsion system with the pre-hydrolyzed silanes, with mechanical agitation, in a reactional balloon; submission of the reactional medium to three temperatures, referred through this work as T1, T2 and T3, while the polycondensation reactions of the pre-hydrolyzed silanes occurs; filtration of the obtained microcapsules; drying of the microcapsules and storage in a moisture-free environment. Further details regarding the experimental base procedure are confidential.

The Fig. 22 presents the laboratorial montage used for the microcapsules syntheses, before the arrival of the heating mantle.

Fig. 22 – Laboratorial set-up used for the microcapsule synthesis

Experimental Results:

The synthesis of silica based microcapsules, 20T:0M:0G, had already been previously made in Greenseal Research. In this work, the referred synthesis was carried out with the purpose of studying its reproducibility, as well as to have more microcapsules available for some further characterization and for comparison with the microcapsules obtained in the following studies.

From the results obtained by SEM, observed in Fig. 23, it is possible to conclude that the silica based microcapsules have an almost perfect spherical shape and can be classified as porous matrix microcapsules. However, it is also possible to observe a large size dispersion, along with some agglomeration. In the Fig. 23, it is possible to observe capsules with diameters of about 30μm as well as with almost 300μm. The existence of agglomerated capsules, as well as their significant size, can lead to obstruction of the spray nozzle, after the first spray. These microcapsules' porosity is visible in Fig. 24.

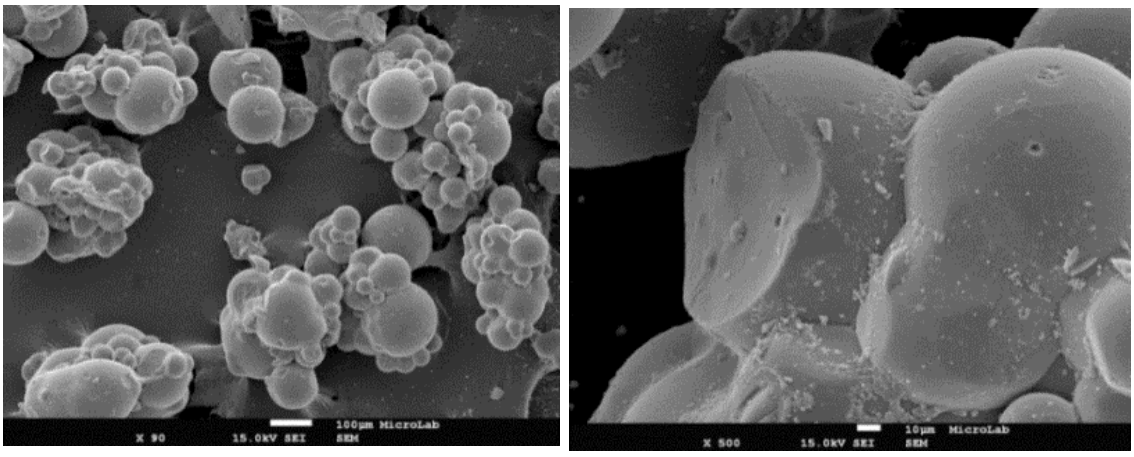


Fig. 23- SEM photomicrographs of 20T:0M:0G microcapsules. A) 90x magnification B) 500x magnification

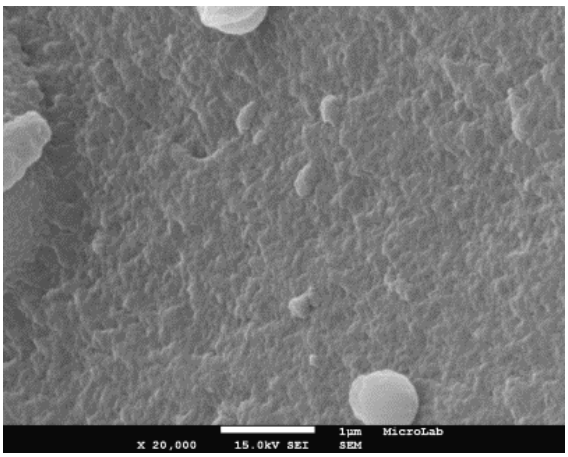
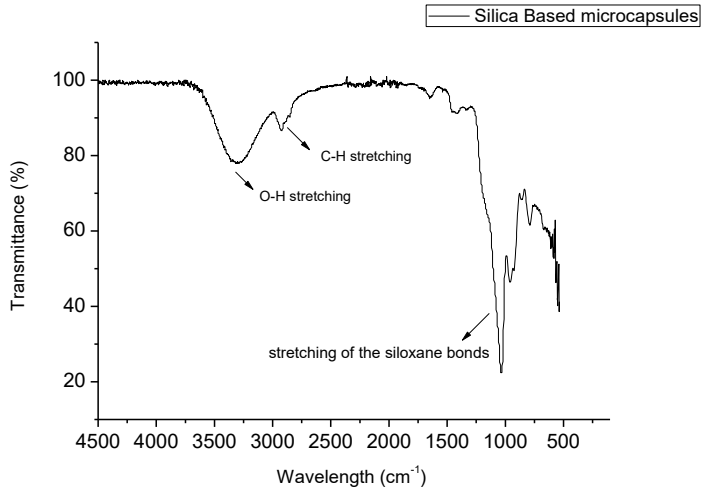


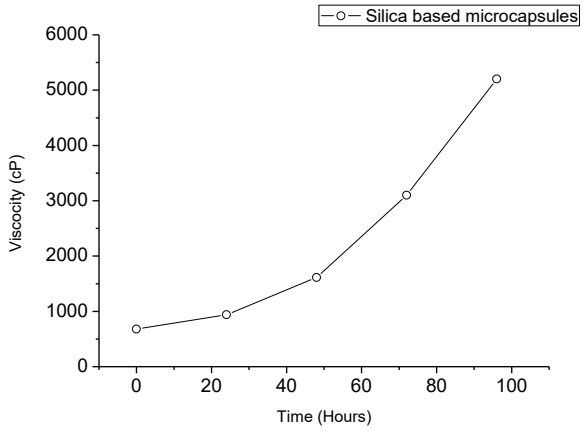
Fig. 24 – SEM photomicrograph of 20T:0M:0G microcapsule cross-section. 20000x magnification

In the Graphic 1 it is presented the FTIR's results for these microcapsules. The broad FTIR band peaked at ca. 3300 cm^{-1} is due to the presence of O-H groups (O-H stretching), derived from the encapsulated glycerol, but also from the existence of some remaining water (inorganic silica is hygroscopic) and possibly some uncondensed silanol groups. Additionally, the peaks at 1640 cm^{-1} and ca. 650 cm^{-1} show the presence of H_2O (HOH bending). Another evidence for the presence of glycerol is the band between ca. 1500 and 1300 cm^{-1}, due to CH_2 and OH bending). The FTIR peaks at ca. 3000-2750 cm^{-1} are ascribed to the C-H stretching in CH_3, CH_2, and CH moieties. The FTIR peak presented at 1070cm^{-1} corresponds to the asymmetric stretching of the siloxane bonds Si-O-Si and its presence is due to the polycondensated TEOS.



Graphic 1 – FTIR spectrum for 20T:0M:0G microcapsules.

From results obtained from the leaching tests it is possible to conclude that a fast release of the encapsulated compound happened. From the Graphic 2 it is possible to verify that, after only 100 hours, the Ongronat® 2500 solution was already very viscous, with a viscosity value of 5000 cP. This high viscosity value can be explained not only by the leaching of the glycerol, but also due to some possible water present in the microcapsules, since the silica is a very hygroscopic material, and may lead to a possible accumulation of superficial water.



Graphic 2 – Leaching test result for 20T:0M:0G microcapsules in Ongronat®2500

The Table 2 shows the results for the shaking rate test of silica based microcapsules in OCF. As it can be seen, after 120 hours, the difference in the shaking rate between the two cans is notorious, with a difference of five values. This confirms that leaching was occurring. This result shows a diminution of the lifetime of the can with the incorporation of the microcapsules.

Table 2 – Shaking rate test results for silica based microcapsules

Synthesis	SR (Shaking Rate)			
	0h	72h	96h	120h
Reference	5	5	3	3
20T:0M:0G	5	4	1	-2

In the Table 3 the results obtained for OCF curing time tests with silica based microcapsules are presented. Although the precise time of the complete curing of the

foam was not measured, an improvement can be viewed, in comparison with the reference, for the foam with microcapsules.

Table 3 – Curing time test results with silica based microcapsules

Synthesis	Curing Rate at 10%RH		
	24h	48h	67h
Reference	-4	-3	-2
20T:0M:0G	-2	0	1

Conclusions:

It was possible to synthetize silica based microcapsules.

The microcapsules have a perfect spherical form, however with some agglomeration, large size dispersion, big dimensions and can be classified as matrix microcapsules.

The glycerol is leaching from the microcapsules without its breaking, leading to a decrease of the can's lifespan.

4.2.2. Synthesis of hybrid microcapsules

For the synthesis of organically-modified (hybrid) microcapsules there were used two to three different precursors per synthesis. The precursors used were TEOS, Methyltriethoxysilane (MTES), and (3-Glycidoxypropyl)methyldiethoxysilane, GPTMS, Fig. 25. The properties of the referred precursors are presented at Table 4.

The MTES and GPTMS silanes were used in combination with TEOS with the purpose of obtaining microcapsules with a more flexible and hydrophobic shell, reducing the leaching that was observed for inorganic silica based microcapsules.

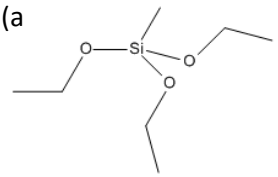
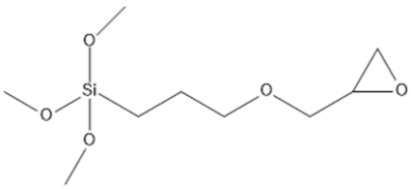
(a  (b 

Fig. 25 – a) Representation of MTES, Methyltriethoxysilane, molecule and b) GPTMS, Glycidoxypropyl Trimethoxysilane, molecule

Table 4 - Precursors used, and their properties, for hybrid microcapsules synthesis

Reagents	Brand	Density (g/ml)	Viscosity (20°C)	Purity grade (%)
Methyltriethoxysilane (MTES)	Dow Corning	0.90	_	99
Glycidoxypropyl Trimethoxysilane (GPTMS)	Dow Corning	0.98	2.9 mPa.s	99
Tetraethyl orthosilicate (TEOS)	VWR Chemicals	0.93	0,72 mm^2s^{-1}	99

For the synthesis of hybrid microcapsules, the experimental procedure adopted was also the experimental base procedure, described in 4.2.1. However, in some cases, it was required to optimize the process and make some modifications, since the polycondensation reaction time differs among the different precursors. The quantity, in grams, of precursors used in each synthesis was maintained and was equal to the amount used for silica based microcapsules.

4.2.2.1. TEOS and MTES microcapsules

Experimental procedure:

There were made three different syntheses with TEOS and MTES: synthesis one: 15T:5MTES:0G; synthesis two: 10T10M:0G; synthesis three: 5T:15:M:0G.

Synthesis one and two had already been previously done in Greenseal Research. The repetitions of these syntheses were made with the purpose of having more

microcapsules for some further characterization, as well as to ensure that the results of the three syntheses were obtained in the exactly same reactional conditions.

In the case of synthesis one, it was necessary a reaction time of 2h30 at T3. For reactions two and three it was necessary to react over night at T3. It is possible to conclude that MTES polycondensation might be slower than TEOS, and so a larger reaction time was needed.

Experimental Results:

SEM characterization was made only for the microcapsules obtained with 10T:10M:0G, i.e. synthesis two, and 5T:15M:0G, i.e. synthesis three.

From Fig. 26 A), it is possible to observe some microcapsules aggregation. Also, it is possible to observe that the microcapsules sizes range between 33μm and 150μm, indicating not only a decrease in the size range distribution but also in the average microcapsules size, when comparing with silica based ones, decreasing the nozzle obstruction possibility. From the Fig. 26 B) it is possible to conclude that the microcapsules obtained from synthesis two are core shell. However, the core size is small in comparison with the diameter of the microcapsule.

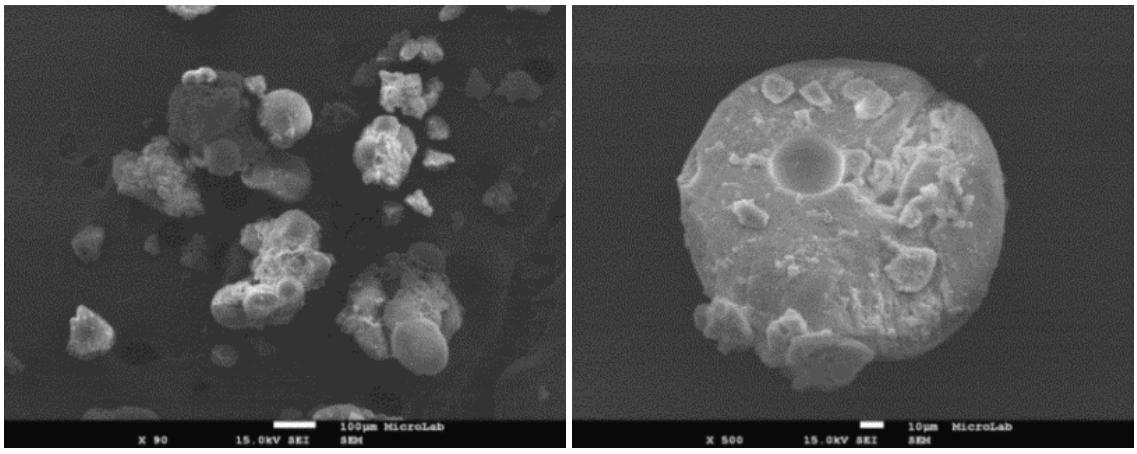


Fig. 26- SEM images of 10T:10M:0T microcapsules. A) 90x magnification B) 500x magnification

From SEM characterization results it is also possible to notice alterations in the shell surface of the hybrid microcapsules, in comparison with silica based ones. Analyzing Fig. 27 it is possible to observe some wrinkling in the hybrid microcapsules surface, that is not visible in the silica based ones. This may be due to water evaporation during the drying process in the oven, during 48 hours at 45°C. In the case of silica based microcapsules, this phenomena is not visible, possibly due do the fact that this capsules are too rigid to wrinkle.

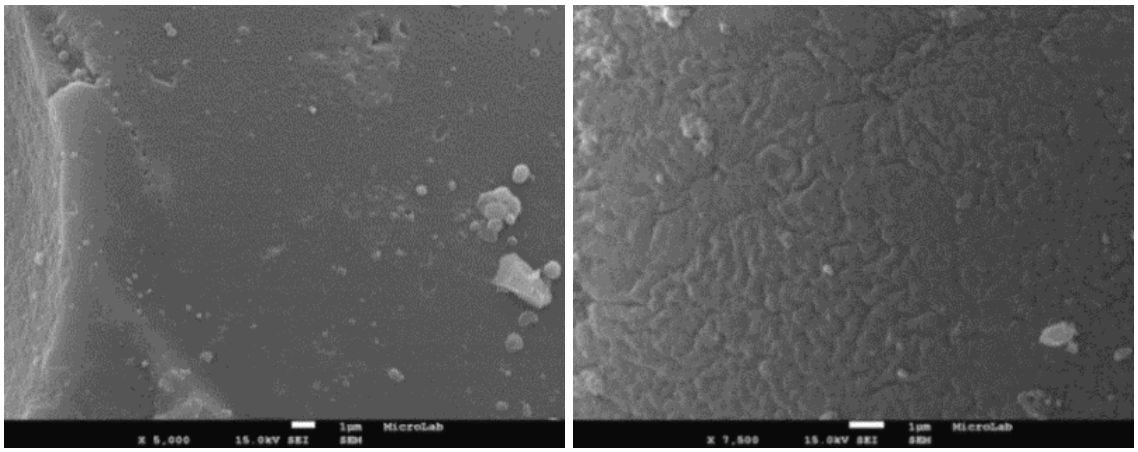


Fig. 27 - A) SEM image of a silica based microcapsule surface, 5000x magnification B) SEM image from 10T:10M:0G microcapsule surface, 7500x magnification

It is also possible to notice alterations in the inner porosity of the hybrid microcapsules, as seen in Fig. 28. The hybrid microcapsules appear to be more porous and to have a larger porosity than the silica based ones. Since the glycerol can also be entrapped in the pores of the inner shell and not only in the core, the apparent increase in the porosity may contribute to encapsulate a greater amount of glycerol.

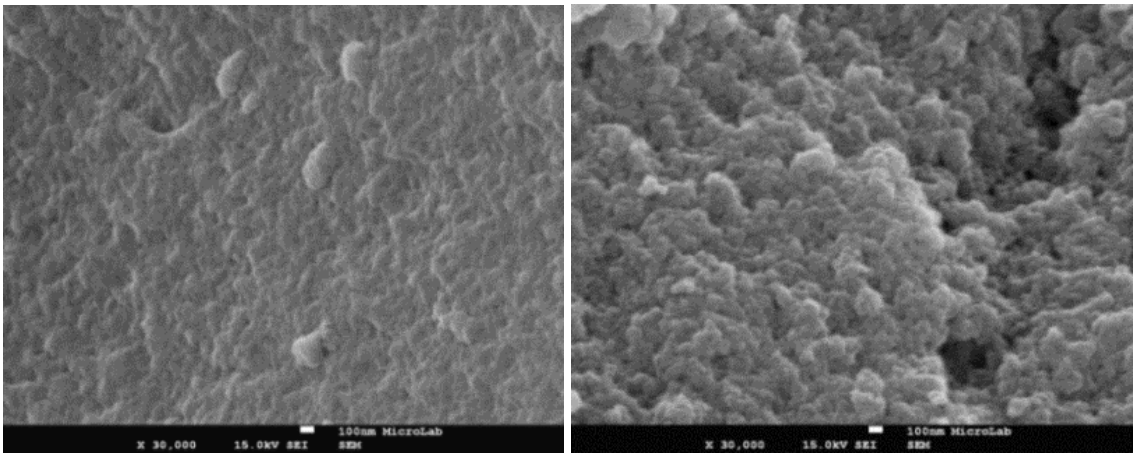


Fig. 28 – A) image of sílica based microcapsule interior, obtained from a microcapsule cross section, 30000x magnification B) SEM image from 10T:10M:0G microcapsule interior, 30000x magnification

As it is possible to observe in Fig. 29, the microcapsules obtained through the synthesis three do not have a perfectly spherical shape, and the majority appears to be broken. Also, they have larger dimensions, in comparison with both silica based and 10T:10M:0G microcapsules having about 700μm (Fig. 29 A). However, this synthesis resulted in poly-nucleated microcapsules, with larger cores, which is a desired factor, since they may allow the encapsulation of a larger amount of glycerol.

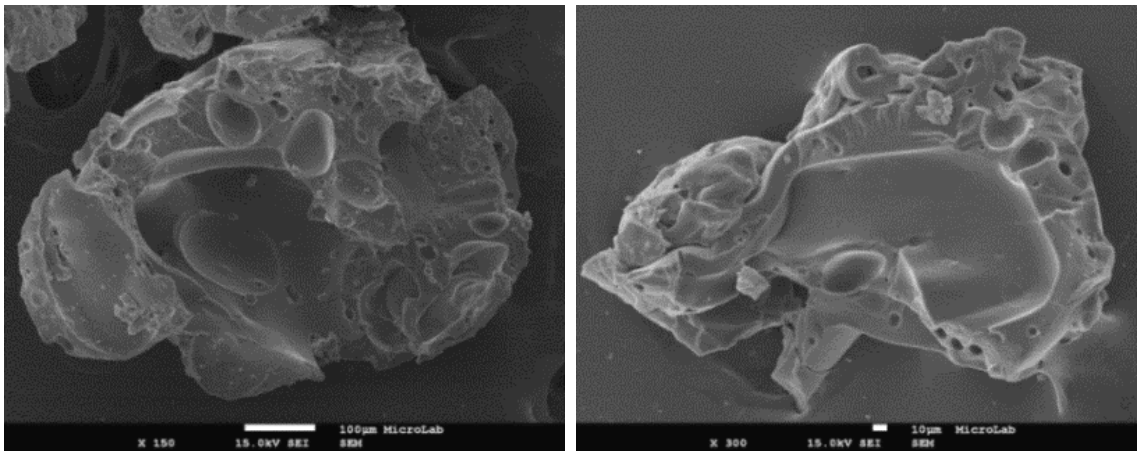
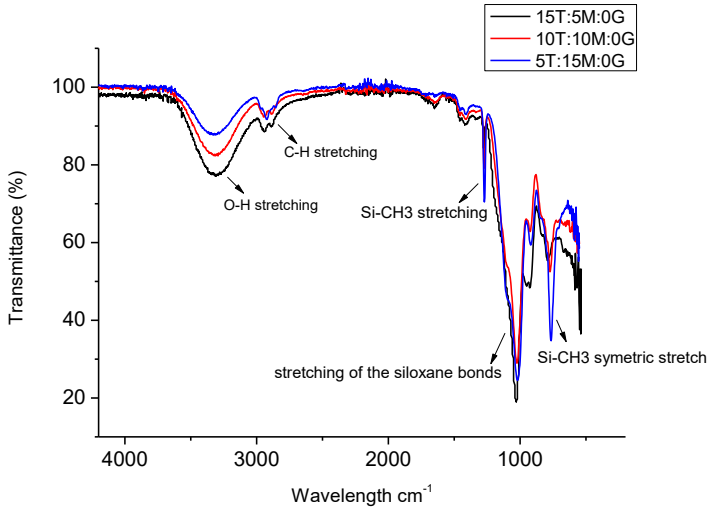


Fig. 29 – SEM images of 5T:15M:0G A) 150x magnification B) 300x magnification

For the results presented in the further characterizations, it is important to note that the majority of the microcapsules obtained in the synthesis three may be broken.

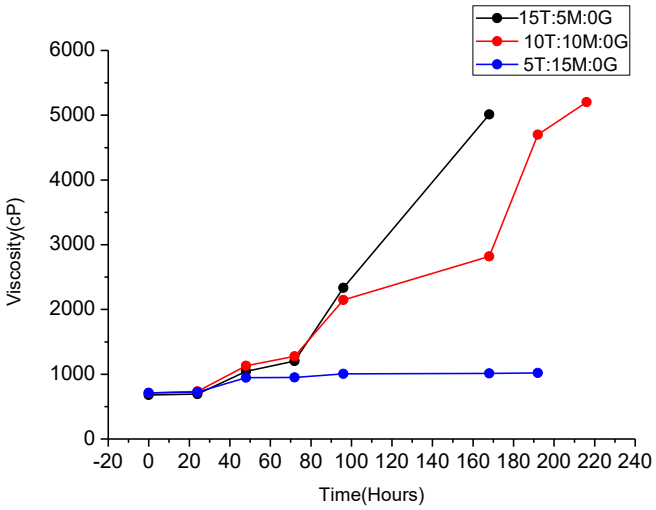
From FTIR characterization, presented in Graphic 3, it is possible to observe that as the amount of MTES in the microcapsules increases, the intensity of O-H band, peaked at ca. 3300 cm^{-1}, decreases, indicating a decrease of water in the system (the band at 1640 cm^{-1} also decreases) and a possible reduction of the encapsulated compound (glycerol). The peak within the range 2750-2900 cm^{-1}, due to C-H stretching in CH_3 moieties, also increases, which is derived from the larger amount of MTES used. It is also visible a band at around 1275cm^{-1} and another at 770cm^{-1}, both related with the presence of the Si-CH_3 group. Also, the intensity of the referred bands rises with the increase of the amount of MTES in the microcapsules. These bands can be a confirmation that this precursor reacted with the hydrolyzed TEOS and, thereby, is present in the microcapsules shell.



Graphic 3 – FTIR results for hybrid microcapsules

From the leaching test results it is possible to conclude that the leaching decreases with the increase of MTES amount used in the synthesis, as can be seen in Graphic 4. The synthesis with 5T:15M:0G does not show a significant leaching, however, as observed by SEM, the majority of this synthesis microcapsules might be broken. Such reduction in the leaching is corroborated by the FTIR results: the reduction in water

observed by FTIR (the more MTES the MCs contain, the more hydrophobic they are), and possibly also some reduction in the encapsulated glycerol content.



Graphic 4 –Leaching tests results for hybrid microcapsules

Table 5 presents the results of the shaking rate test, obtained with the microcapsules synthetized with TEOS and MTES silanes**.** As it can be seen, the results obtained with these microcapsules are not very different from the ones obtained with the reference foams, i.e., the foam without microcapsules. Comparing with the shaking rate results obtained with silica based microcapsules, presented in Table 2, it is possible to verify that there was a decreasing in the leaching in OCF cans with the microcapsules synthetized with MTES.

Table 5 – Shaking rate test results for microcapsules with MTES

Synthesis	SR (Sharking Rate)			
	0h	72h	96h	120h
Reference foam	5	5	3	3
15T:5M:0G microcapsules	5	4	3	3
10T:10M:0G microcapsules	5	4	4	4

The Table 6 presents the results of the curing time test with microcapsules synthetized with TEOS and MTES. Although the precise time of the complete curing of the foam was not measured, an improvement in the results can be verified. The test results obtained for the foam with 10T:10M:0G microcapsules are very similar to the ones obtained with the silica-based microcapsules.

Table 6 – Curing time test results for microcapsules with MTES

Synthesis	Curing Rate at 10%RH		
	24h	48h	67h
Reference	-4	-3	-2
15T5M:0G microcapsules	-3	-1	0
10T:10M:0G microcapsules	-3	0	1

Table 7 presents the results obtained for string, tack free and cutting time tests for OCF with 10T:10M:0G microcapsules. As it can be seen, the string time result was not affected by the presence of the microcapsules. Regarding tack free and cutting times, some difference was observed between the results obtained with and without the microcapsules. A decrease by half in the tack free time was observed in comparison with the reference and, in the case of the cutting time, an improvement of one hour was perceived, which corresponds to an improvement of 40%, when comparing with the reference results.

Table 7 – Tring, tack and cutting time tests results for microcapsules with MTES

Synthesis	String Time	Tack free Time	Cutting Time
	Seconds	Minutes	Minutes
Reference	120	39	150
10T10M:0G microcapsules	120	20	90

Conclusions:

It was possible to synthetize microcapsules with TEOS and MTES precursors in particular higher quantities of MTES (10 and 15g MTES within 20 grams total of silanes), which is not reported in the literature up to the moment.

The microcapsules 10T:10M:0G showed the best compromise between quality/morphology, leaching and curing speed.

Comparing to the reference foam (without microcapsules) the tack free time was reduced by half the time and the cutting time was reduced by 40%.

4.2.2.2. TEOS and GPTMS microcapsules

Experimental Procedure:

Two different syntheses were conducted with TEOS and GPTMS; Synthesis one: 15T:0M:5G; Synthesis two: 10T:0M:10G.

For the first synthesis there was no need for alterations to the experimental base procedure. In the case of the second synthesis, was necessary a reaction time of 2h at T3 for the polycondensation to fully occur.

Experimental Results:

SEM characterization was made only for the microcapsules obtained through the second synthesis, 10T:0M:10G. It is possible to observe, from Fig. 30 A) that the microcapsules obtained through the referred synthesis do not have a spherical form. Instead, they appear to have an irregular shape, interconnected morphology. From Fig. 30 B), it is possible to verify that the shell surface appears to have slight circular depressions, which differs from both silica based and MTES microcapsules. The microcapsules diameters vary between about 70μm to almost 300μm, a larger range than in the case of microcapsules synthetized with MTES.

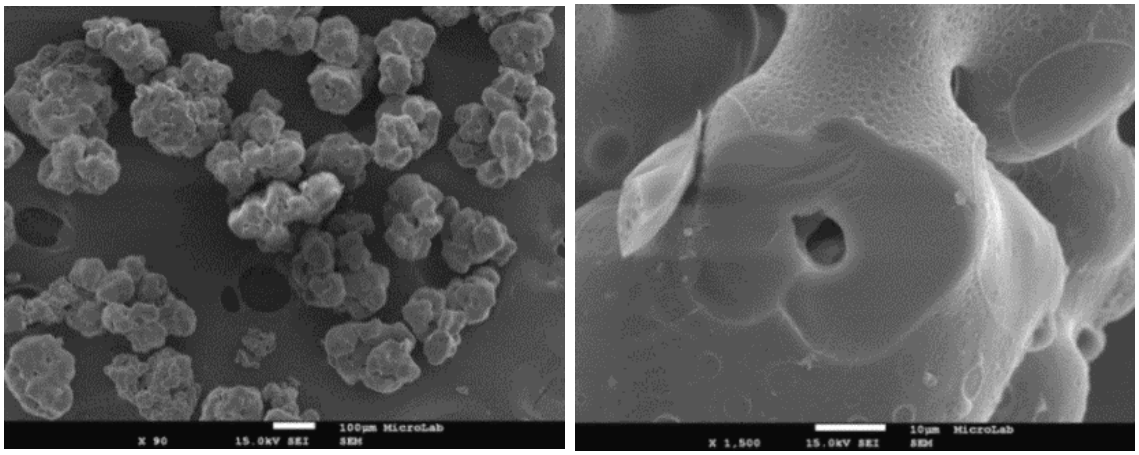


Fig. 30 - SEM images of 10T:0M:10G microcapsules. A) 90x magnification B) 1500x magnification

From SEM characterization it was also possible to conclude that the interior of the microcapsules 10T:0M:10G, Fig. 31 A), shows more similarity to the interior of silica based ones than to 10T:10M:0G, since they seem to have a low porosity.

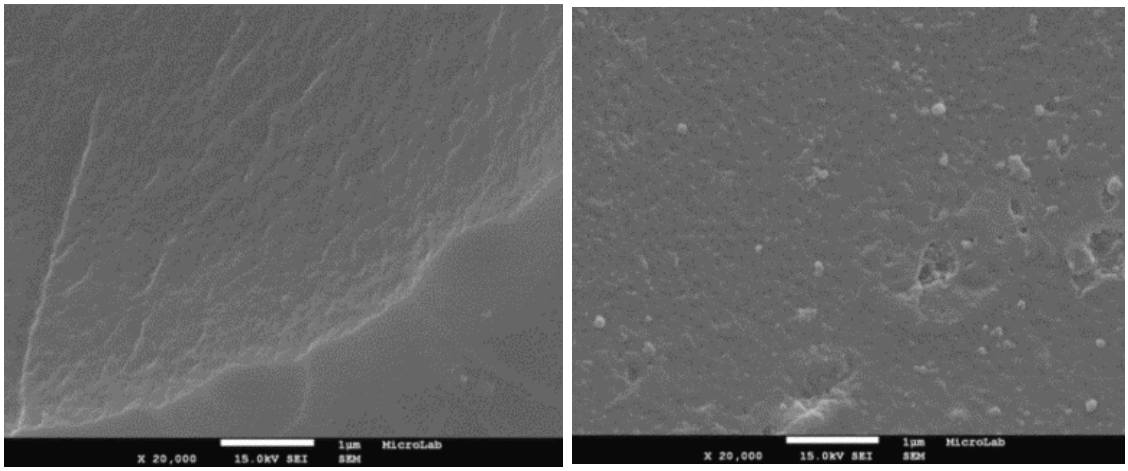
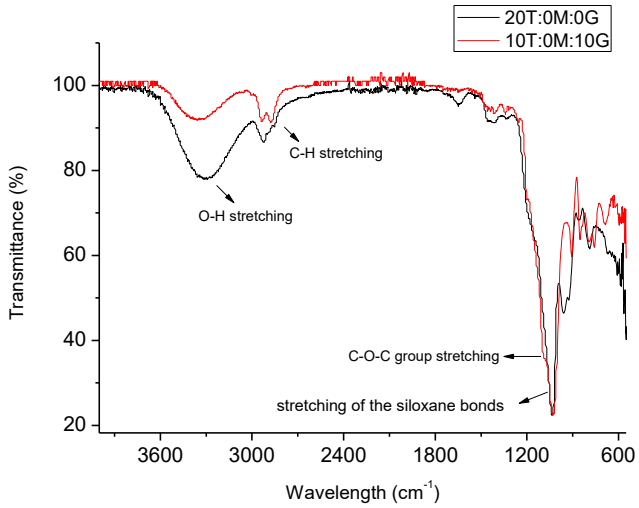


Fig. 31 – A) SEM image of 10T:0M10G microcapsules interior, 20000x magnification B) SEM image of sílica based microcapule interior, 20000x magnification

FTIR characterization was only made for 10T:0M:10G synthesis; therefore the results will be compared with the ones obtained for silica based microcapsules. From Graphic 5 it is possible to observe a broad band (OH stretching) peaked at ca. 3300 cm^{-1}, for 10T:0M:10G, which is much less intense than in the case of inorganic silica microcapsules. Also, the peak at 1640 cm^{-1} and the bands between ca. 1500 and 1300

cm^{-1} also decrease, which means that there is less water moieties and less glycerol in these capsules. From the Graphic 5 it is also possible to observe a shoulder at around $1097cm^{-1}$, in the band located at ca. $1000cm^{-1}$, presented only in the FTIR results for microcapsules with the GPTMS silane. This is due to the presence of the C-O-C group, which has stretch bands located between $1050cm^{-1}$ and $1150\ cm^{-1}$. Also there is a small peak at $915\ cm^{-1}$ and $831\ cm^{-1}$, ascribed to C-O and C-O-C stretching of the epoxy (oxirane) groups of GPTMS, which reveals that the epoxy groups are still present in the microcapsule shell and there was no ring opening polymerization phenomenon occurring.



Graphic 5- FTIR results of 10T:0M:10G as well as of silica based microcapsules

In Table 8 the principal results obtained through the TGA analysis are presented. The respective TGA thermogram is presented in Appendix D, Fig.D 2. The percentage of mass lost until 300°C was calculated, since, from the TGA thermogram of the glycerol, presented in appendix D, Fig.D 1, it can be seen that its loss occurs until the referred temperature. Besides the glycerol loss, some water loss can also be visible, which is presented in the Table 8.

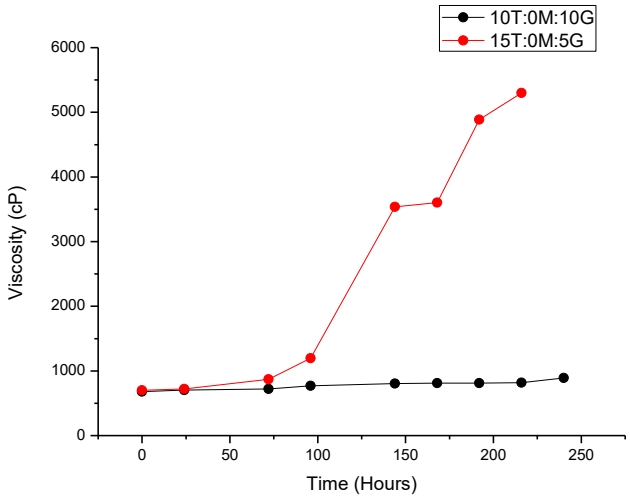
From Table 8, it can be seen that the microcapsules synthetized with 10T:0M:10G do not have a high amount of encapsulated compound, since they only seem to have

about 17,87% in mass of glycerol, which is a small amount of the overall microcapsules' weight.

Table 8 –TGA analysis results of microcapsules synthetized with 10g of TEOS and 10g of GPTMS

Onset Temperature,°C	Average Temperature,°C	% of mass lost until 300°C	% of water
185,51	257	19,6	1,73

In the Graphic 6 is represented the leaching results. As it is possible to observe, there was a decreasing in the leaching with the increase of GPTMS amount used in the syntheses. The Ongronat® 2500 with these microcapsules barely showed any increasing in viscosity. However, comparing with the results obtained from FTIR characterization, it is possible that the decreasing in leaching observed in this synthesis may be due to a reduced amount of encapsulated glycerol.



Graphic 6 – Leaching test result of hybrid microcapsules with GPTMS

The Table 9 shows the results obtained for the shaking rate test with 10T:0M:10G microcapsules in OCF**.** As can be seen even after 120 hours, there is no difference in the shaking rate between the reference can and the one with microcapsules. This result indicates that there was a decreasing in the leaching in comparison with silica based microcapsules.

Table 9- Shaking rate tests results of 10T:0M:10G

Synthesis	SR (Sharking Rate)(hours)			
	0	72	96	120
Reference	5	5	3	3
10T:0M:10G microcapsules	5	4	3	3

The Table 10 presents the results of the curing time test for 10T:0M:10G microcapsules in OCF. Although the precise time for the complete curing of the foam was not measured, it can be seen there were no significant improvement in the curing time of the foams with this microcapsules. When comparing with the results obtained from silica based ones it is possible to conclude that the 10T:0M:10G microcapsules have less effect in the curing of the foam, in line with the fact that these capsules exhibited less glycerol encapsulated (in the FTIR spectrum).

Table 10 –Curing time test results with 10T:0M:10GP microcapsules

Synthesis	Curing Rate at 10%RH		
	24h	48h	67h
Reference	-4	-3	-2
10T:0M:10G microcapsules	-3	-1	-1

The results obtained for string, tack free and cutting time with 10T:0M:10G microcapsules in OCF foams are presented in the Table 11. Comparing with the results obtained for the reference, it is possible to say that, for all the parameters studied, there was an improvement in the results obtained with the application of the microcapsules in the foam. A reduction of the cutting time by 40% was observed.

Table 11 – String, tack and cutting time results of 10gTEOS 10g GPTMS microcapsules

Synthesis	String Time	Tack free Time	Cuting Time
	Seconds	Minutes	Minutes
Reference	120	39	150
10:T:0M:10G microcapsules	60	24	90

Conclusions:

It was possible to synthetize microcapsules with TEOS and GPTMS.

The obtained microcapsules do not have a perfectly spherical shape and have a large diameter range when comparing with the microcapsules obtained with MTES.

These microcapsules showed a decreasing in the leaching, in comparison with the silica based ones and did not influence the shaking rate.

4.2.2.3. TEOS, MTES and GPTMS microcapsules:

Experimental Procedure:

Two different syntheses were made with the TEOS, MTES and GPTMS precursors; Synthesis one: 5T:10M:5G, synthesis two: 5T5M:10G. The first synthesis had already been previously done in Greenseal Research. Its repetition was made with the purpose of having more microcapsules for some further characterization as well as to ensure that all the results of this study were obtained in the exactly same reactional conditions.

In the case of the first synthesis it was necessary that the reaction remained at T3 during the night. For the second synthesis it was only needed that the reaction remained at T3, for 3h30.

Experimental Results :

- **5T:10M:5G:**

It is possible to observe that microcapsules obtained with 5T:10M:5G do not have a perfect spherical form, instead they have an irregular shape, Fig. 32 A). In Fig. 32 B) it is possible to observe the inside of a broken microcapsule, which seems composed by several agglomerated microcapsules. From Fig. 32 A) it is also possible to observe that

the microcapsules have diameters ranging from about 50μm to 250μm, which is a smaller range size when compared with silica based ones.

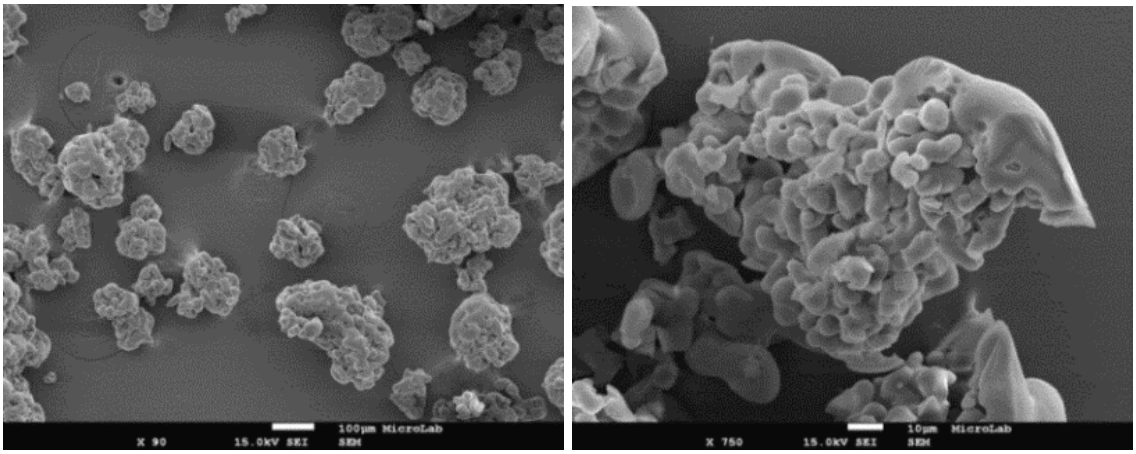


Fig. 32 – SEM images of 5T:10M:5G microcapsules. A) 90X magnification B) microcapsule interior, 750x magnification

In Fig. 33 it is possible to observe a transversal section of the microcapsules, showing the agglomerates in the inside. As it can be seen, they have a low porosity. The interior seems similar to the ones obtained with silica based microcapsules. It is also observable some circular depressions (interconnected morphology) in the surface of this microcapsules, as was also observed in the ones synthetized with 10T:0M:10G.

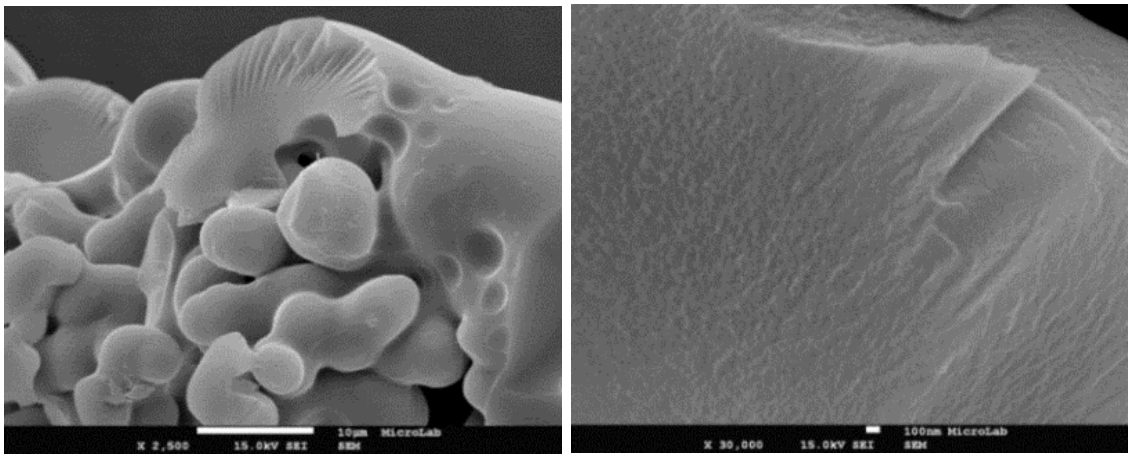


Fig. 33 – SEM images of 5T:10M:5G interior. A) 2500x magnification B)30000x magnification

- **5T:5M:10G:**

The microcapsules obtained with 5T:5M:10G do not have a spherical shape, as seen in Fig. 34. Instead, they seem to be composed by several microcapsules that, at some point during the synthesis, suffered coalescence.

These microcapsules have bigger dimensions, when comparing with the 5T:10M:5G ones. As it is visible in Fig. 34 A), they have about 400μm and 700μm of diameter. As seen from Fig. 34 B), the capsule surface has several circular depressions which was also visible in the previous synthesis, although in a smaller amount. In all the synthesis with GPTMS, this type of circular depressions on the surface was observed.

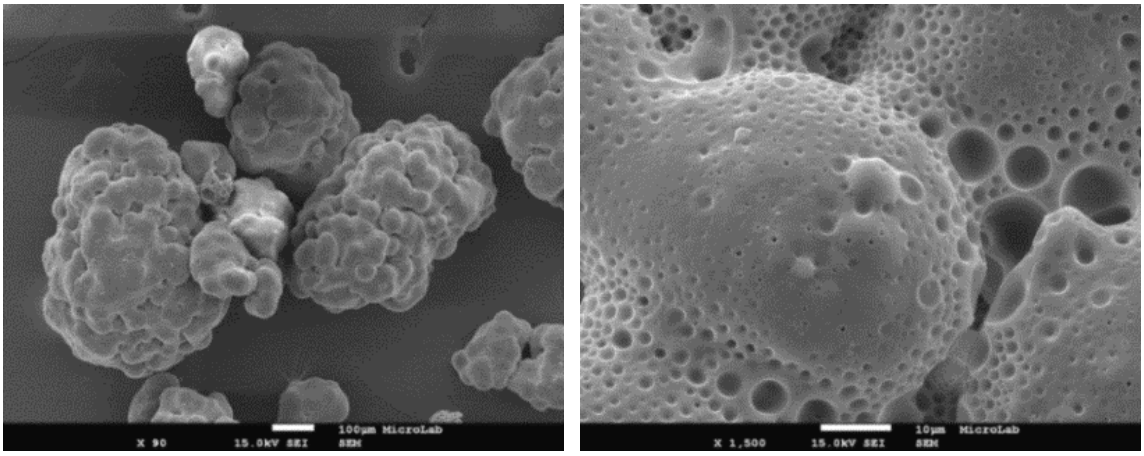
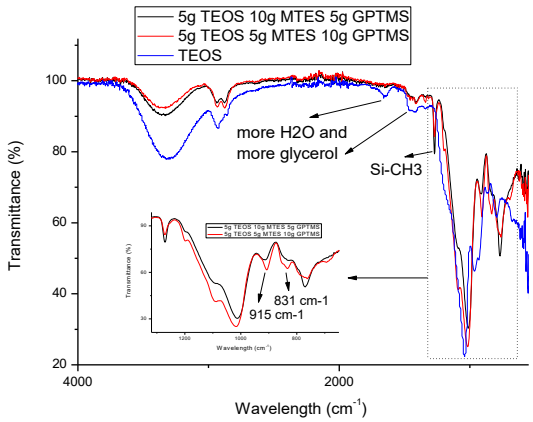


Fig. 34 – SEM images of 5T:5M:10G. A) 90xmagnification B) 1500x magnification

In Graphic 7, the FTIR results obtained for the microcapsules synthetized with TEOS, MTES and GPTMS precursors are presented, as well as the results obtained for silica based microcapsules. As it can be seen, the O-H band, visible at ca. 3300 cm^{-1}, is 14% more intense in the silica based spectra, compared to the transmittance registered for 5T:5M:10G microcapsules, and 12% more intense when compared to 5T:10M:5G microcapsules FTIR spectra. It is also possible to observe that, the more GPTMS used in the synthesis, the lower the intensity of the O-H band.

In MTES derived microcapsules the bands corresponding to the Si-CH_3 group are also visible, at 1275cm^{-1} and 770cm^{-1}. As expected, these bands have a slightly higher

transmittance intensity for the synthesis with more MTES. On the other hand, the bands corresponding to the presence of the epoxy ring for GPTMS derived capsules are also detected for the corresponding samples (the inset in Graphic 7).



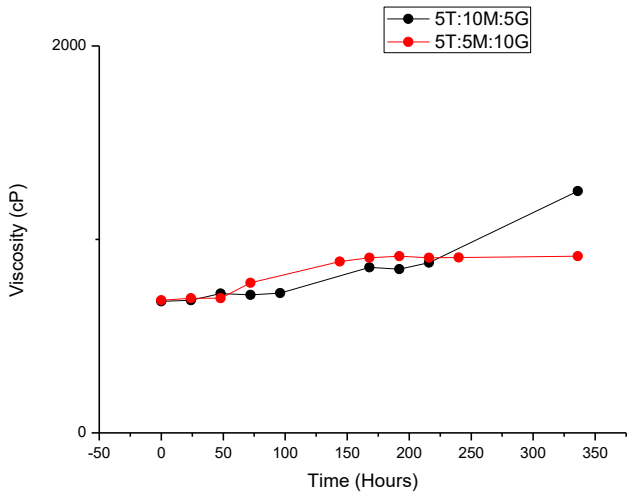
Graphic 7 - FTIR results of 5T:10M:5G, 5T:5M:10G and silica based microcapsules

From TGA analysis, with the results presented in Table 12 and the respective thermogram in the appendix D,Fig.D 3 , it was possible to conclude that only 15,87% of the total weight of 5T:5M:10G microcapsules corresponds to encapsulated glycerol. When comparing with the results obtained from the TGA for the microcapsules synthetized with 10T:0M:10G, it is possible to conclude that the ones obtained in this study have a lower percentage of both encapsulated glycerol and water, with a difference of 2% and 0,34% respectively.

Table 12- TGA results obtained with 5T:5M:10G microcapsules

Onset Temperature,°C	Average Temperature,°C	% of mass lost until 300°C	% of water
159	259	17,26	1,39

The leaching results for the microcapsules composed of TEOS, MTES and GPTMS silanes are represented in Graphic 8. As it can be seen, there was no significant increase in the viscosity of Ongronat® 2500 in the 350h range. The synthesis with more GPTMS had, after the 350 hours, the lowest leaching value. However, it may be due to a lower amount of glycerol encapsulated, as concluded from Graphic 7.



Graphic 8 – Leaching test results for microcapsules synthetized with TEOS, MTES and GPTMS

The results for the shaking rate test are presented in the Table 13. As it can be seen, the difference between the reference and the microcapsules obtained in this study is not significant, indicating that there was a decreasing in leaching in comparison with silica based microcapsules. However by FTIR, it was observed that the hybrid microcapsules also have less glycerol encapsulated.

Table 13 – Shaking rate test results of microcapsules synthetized with TEOS, MTES and GPTMS

Synthesis	SR (Shaking Rate)(horas)			
	0h	72h	96h	120h
Reference	5	5	3	3
5T:10M:5G microcapsules	5	4	4	-
5T:5M:10G microcapsules	5	4	4	3

The results of the test of curing time with the microcapsules composed of TEOS, MTES and GPTMS silanes are presented in the Table 14. Although the precise time of the complete curing of the foam was not measured, it can be seen that, the microcapsules

with more amount of MTES seems to have a more significant effect on the curing of the foams, than the ones with more GPTMS, although this difference is not very significant.

Table 14 – Curing time test results for TEOS,MTES,GPTMS microcapsules

Synthesis	Curing Rate at 10%RH		
	24h	48h	67h
Reference	-4	-3	-2
5T:10M:5G microcapsules	-3	-2	0
5T:5M:10G microcapsules	-3	-2	-1

Conclusions:

It was possible to synthetize microcapsules with the three combined precursors, TEOS, MTES and GPTMS, for the first time, to the best of our knowledge.

The obtained capsules do not have a perfect spherical form, instead they have an irregular shape and seem to be composed by several agglomerated microcapsules.

GPTMS and MTES contribute to some destabilization of the emulsion which affects the morphology of the capsules and the glycerol encapsulation efficiency. Probably, due to this fact there was no significant improvement in the curing speed, with these microcapsules.

4.2.3. Study of reaction parameters

In this chapter, some of the studies made during this work regarding to some reactional parameters will be described. These studies were carried out with the purpose of finding the optimal reactions conditions for the microcapsules' synthesis.

The studied parameters were: the addition of a catalyst, the amount of surfactant used in the synthesis and the possibility of using two type of surfactants; i.e. with W/O emulsifier and O/W emulsifier. The need of a previous hydrolysis reaction of the

silanes was also studied and finally the possibility of increasing the amount of encapsulated glycerol.

4.2.3.1. Catalyst:

The main purpose of this study was to lower the cost of future microcapsules production at a large scale, by decreasing the time of reaction. With the use of a catalyst, the period of time necessary to apply heating decreased, also, this reaction alteration may allow a future increase in the production scale, since more microcapsules can be produced in the same amount of time.

For this study an acidic catalysis was used; hydrofluoric acid, HF. The catalyst properties are present at Table 15.

The syntheses chosen for this study were the one with 10T:10M:0G, since it is the synthesis that requires more reaction time, and the one with 10T:0M:10G, in continuation with the previous study, 4.2.2.1, as a new attempt to diminish the price production of this synthesis.

Table 15- HF properties

Reagents	Brand	Density (g/ml)	Viscosity (mPaS) (20°C)	Purity grade (%)
Hydrofluoric Acid (HF)	Riedel-de Haën	1,15	0.9810	40

Experimental procedure:

In these syntheses, the microcapsules were not subjected to heating at T3. After one hour reacting at T2, three droplets of HF were added to the reaction. The HF was let to react during one minute, after which another three droplets were added to the solution.

The "reference", in this study, are the equivalent synthesis, i.e. 10T:0M:10G and 10T:10M:0G, without the HF addition.

Experimental results:

In both syntheses, after the addition of the three droplets of HF, the microcapsules were formed almost instantaneously. However, in both cases the synthesis' yield was significantly lower. In the case of 10T:0M:10G(+HF) synthesis, a decrease of about 14,94% was observed and, in the case of 10T:10M:0G(+HF), of about 12.89% in the reaction yield, when comparing with the respective references.

The FTIR results obtained for these syntheses confirm the presence of encapsulated material. The FTIR spectrum is presented in appendix B, Fig.B 1. However, it is not conclusive regarding the amount of glycerol encapsulated in the microcapsules obtained through catalyzed syntheses in comparison with the non-catalyzed ones. In one case of 10T:0M:10G (+HF) microcapsules, the O-H broad band is more intense for the microcapsules obtained through the catalyzed synthesis. For the 10T:10M:0G synthesis, the O-H band of the reference is more intense.

Conclusions:

The synthesis of microcapsules with an acidic catalyst is a possibility; the addition of a catalyst has led to an instantaneous microcapsule formation, as desired, and it was confirmed that glycerol was encapsulated.

The yield decreased significantly when the catalyst was used, in comparison with the reference.

More studies might be needed to obtain the optimal reaction conditions for the microcapsules' synthesis with the addition of a catalyst.

4.2.3.2. Surfactant

In the first study of this chapter, the amount of surfactant used for the emulsion formation was increased, as a possibility to obtain a better emulsion stability and to avoid aggregated and big sized microcapsules. The syntheses chosen for this study

were the ones with 10T:10M:0G and with 5T:15M:0G, since the microcapsules obtained through them were aggregated.

In the second study, the possibility of using two different types of surfactant, W/O and O/W, for the emulsion formation was investigated. This study was carried out with the surfactants SPAN 80,Fig. 35, and DC193, Fig. 36, with the respective characteristics presented in Table 16. The synthesis chosen was the 20T:0M:0G. With this alteration, smaller microcapsules were hoped to be obtained, as well as with a narrower diameter range.

Table 16- SPAN80 and DC193 principal characteristics

Reagents	Brand	Density (g/ml)	Viscosity (20°C)	Purity grade (%)	HLB
SPAN80	Merck	0.93	≈1200 mPas	99	4.3
DC193	Dow Corning	1,07	260cSt	_	12

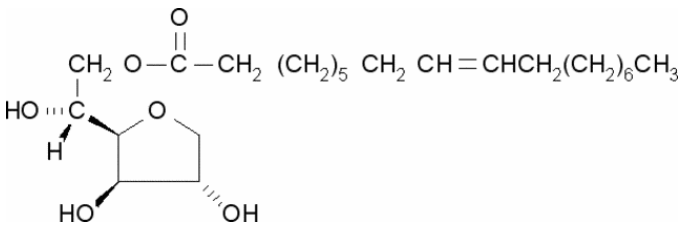


Fig. 35 - SPAN 80 molecule

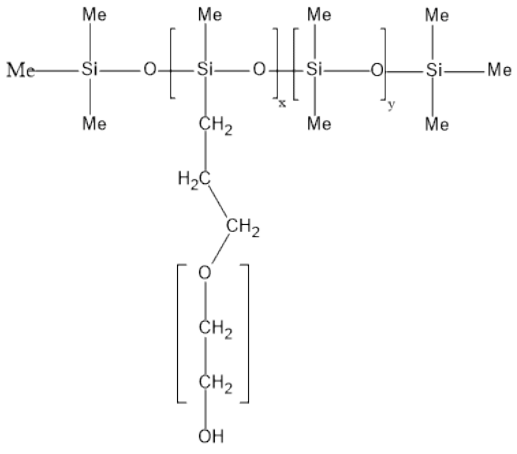


Fig. 36- DC193 molecule

4.2.3.2.1. Surfactant quantity

Experimental procedure:

In this study, the amount of surfactant used was increased by 1/2 in comparison with the amount used in the experimental base procedure. Being so, for the emulsion formation, 3g of SPAN 80 was used instead of 2g. The reactions were also subjected to heating at T3 for more than an hour, since, as already discussed, the syntheses with MTES require more reaction time.

The "references", in this study, are the equivalent synthesis, i.e. 10T:10M:0G and 5T:15M:0G, in which the emulsion was formed with only 2g of SPAN 80.

Experimental results:

The surfactant increase in the synthesis with 10T:10M:0G(+ surfactant) did not lead to microcapsule formation. More than one attempt was made however with no positive results.

Two syntheses with 5T:15M:0G(+surfactant) were made. The reaction yields were lower than the ones of the reference syntheses, with a decrease of 6% and 4.84%. In the Fig. 37 the SEM results for the microcapsules obtained in the two syntheses of this study are presented. As it can be seen, in both cases all the microcapsules appear to be broken.

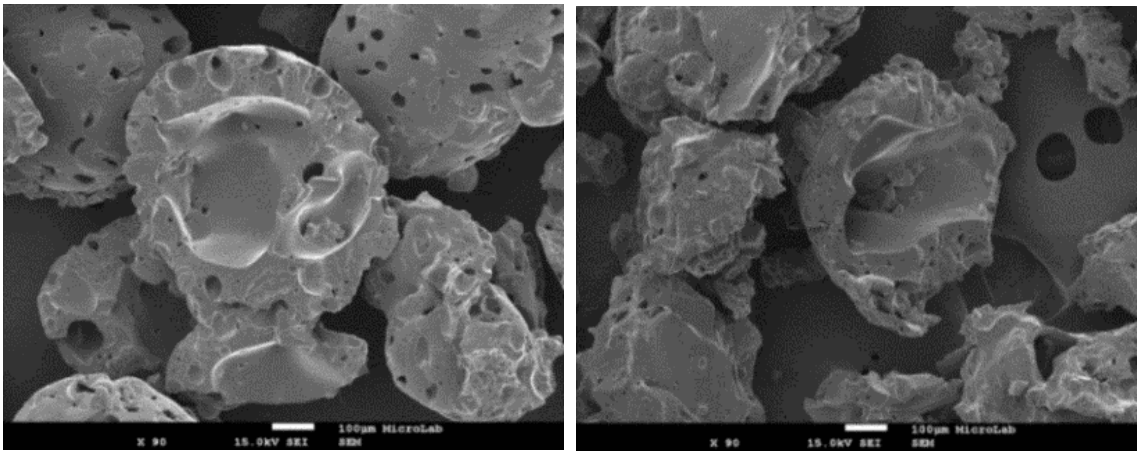


Fig. 37 – SEM of 5T:15M:0G(+surfactant) microcapsules. A)100x magnification B) 90x magnification

By comparing the SEM results of the microcapsules obtained in this study with the reference ones, Fig. 38, it can be seen that, in both cases the microcapsules appear to be core shell. Despite the fact that the microcapsules are still broken, they have smaller sizes and, it seems, a more spherical form. One major difference observed in the microcapsules synthetized with more amount of SPAN80 is the existence of more holes in the surface of the shell.

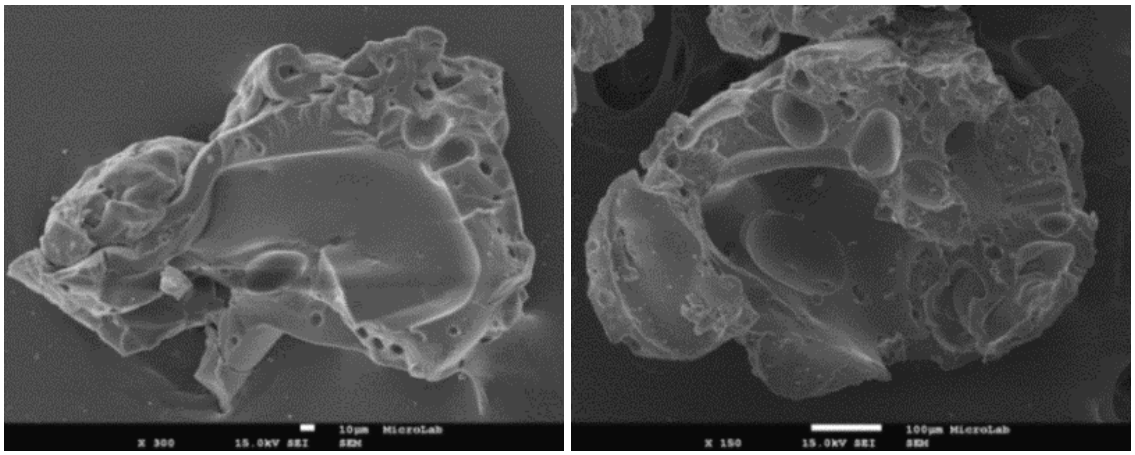


Fig. 38 – SEM characterization of the reference microcapsules (5T:15M:0G microcapsules, with 2g of SPAN80) A) 300 x magnification B) 150x magnification

Conclusions:

The increase of the surfactant amount contributed to a decrease of the microcapsules' size, as well as for the formation of microcapsules with a more spherical shape.

In the case of the synthesis with 10T:10M:0G(+surfactant), it was not possible to obtain microcapsules.

For the synthesis with 5T:15M:0G(+surfactant), all the microcapsules seemed to be broken and showed more holes in the shell surface, when comparing with the reference ones.

4.2.3.2.2. Use of two surfactants

Experimental Procedure:

In this study, two different surfactants were used, SPAN 80 and DC193, with the principal characteristics presented in Table 16. The two surfactants have different HLB values, SPAN 80 is a W/O emulsifier, while the DC193 is an O/W emulsifier. Being so, the SPAN 80 (lower HLB value) was added to the oil phase and the DC193 (higher HLB value) was added to the water phase. The total amount of surfactant used in this study was equal to the amount used in the experimental base procedure; instead of 2g of SPAN 80, it was used 1,5g g of SPAN 80 and 0,5g of DC193.

The "reference", in this study, are the equivalent synthesis, i.e. 20T:0M:0G, for which the emulsion was formed only with one surfactant, SPAN 80.

Experimental results:

Two syntheses with 20T:0M:0G(2 surfactants) were made. After the filtration step, the microcapsules were observed under optical microscope. The results obtained in the two syntheses were not similar, since the microcapsules obtained in the second one

seemed more immature and aggregated, not with a loose powder appearance, as the ones obtained in the first synthesis, as seen in Fig. 39.

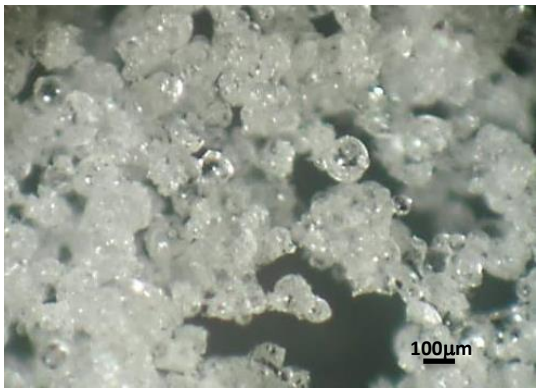


Fig. 39- Photograph taken under optical microscope. The microcapsules were subjected to 45°C heating for 48h

In the Fig. 40, it is possible to observe the SEM images of the same microcapsules presented in the Fig. 39.

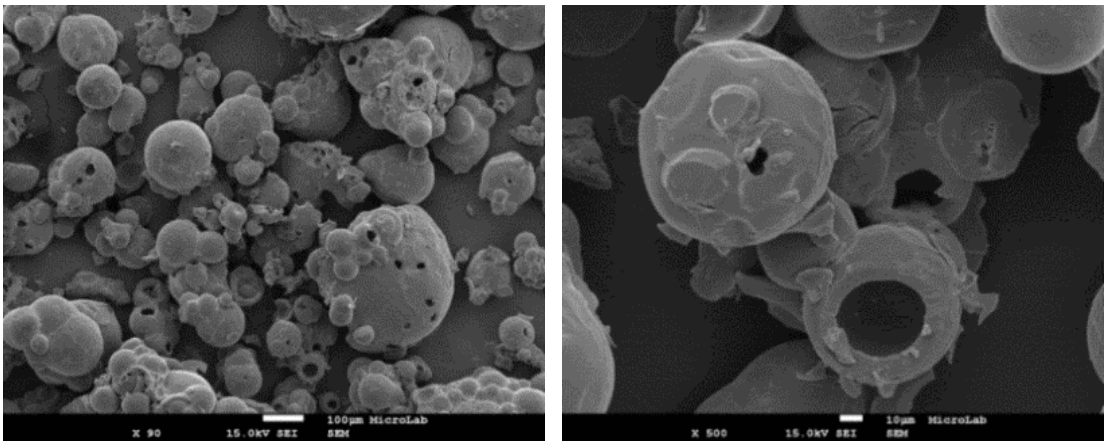


Fig. 40- SEM images of silica based microcapsules with two surfactants A) 90x magnification B) 900x magnification

Comparing with the reference, Fig. 41 it can be seen that the spherical form of the microcapsules was maintained, as well as its aggregation, which was hoped to have decreased. However, one significant improvement was observed in microcapsules obtained in this study; they were core shell microcapsules, which is a desired characteristic. Another alteration observed was the holes in the shell surface, which may lead to an eventual loss of the encapsulated material, however these might have

been formed during the sample preparation for the SEM analysis and/or at the vacuum chamber of the equipment.

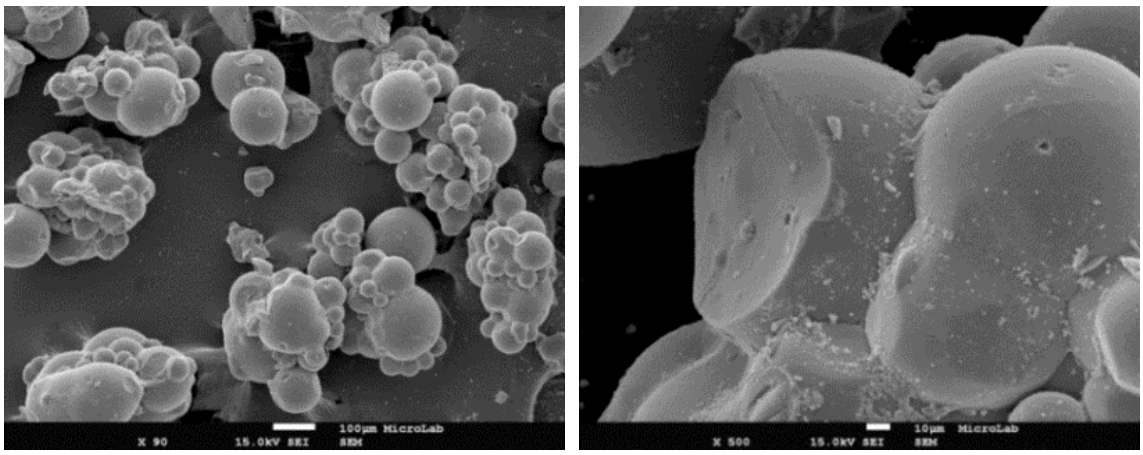


Fig. 41 – SEM images of reference microcapsules A) 90x magnification B) 500x magnification

From the FTIR results, presented in appendix B, Fig.B 2, it was possible to observe that the intensity of the microcapsules' O-H bands obtained with two surfactants is similar to the reference microcapsules. It was expected, from core shell microcapsules, that the amount of glycerol encapsulated would be higher. However, since the microcapsules appear to be broken, this result may not be representative of the storage capacity of these capsules.

Conclusions:

The use of two surfactants for the emulsion formation has showed both negative and positive results:

The microcapsules obtained were core shell, which can contribute to a higher amount of encapsulated glycerol;

However, holes were observable in the shell surface, which may lead to a loss of the encapsulated compound. It was hoped that, with this alteration, the microcapsules aggregation would decrease, which was not observed.

4.2.3.3. Hydrolysis

In this study the need for a previous hydrolysis reaction was tested, replacing this step with the addition of acidic water in the aqueous phase of the emulsion. Being so, the silanes would hydrolyze as the contact with the water phase was made.

The final purpose of this alteration was to obtain core shell silica based microcapsules. This study was based on the article "*Preparation of Mannitol@Silica core–shell capsules via an interfacial polymerization process from water-in-oil emulsion*" [37], where it is stated that it was possible to synthetize core shell microcapsules without the pre-hydrolysis step, since the shell growth that occurs outside-in regarding to the emulsion droplets, stops when the shell is too compact for the precursor to penetrate inside.

Experimental procedure:

For the Sol-Gel technique to succeed, it is necessary that the precursor undergoes successive hydrolysis and condensation reactions. However, in this study, instead of a previous hydrolysis reaction step, the precursor was directly added to the emulsion, while at T1 subjected to mechanical agitation. The water used for the emulsion formation was the acidified water that was used for the pre-hydrolysis reaction step in the experimental base procedure. In this study, the precursors should hydrolyze when in contact with the acidified water present in the emulsion droplets.

The amount of time at which the syntheses reacted under T3 increased was increased. Two syntheses were made, in one case 1h30 at T3 was needed while for the other it was necessary 2h00. The need for more reaction time can be explained by the fact that the silane precursor is not yet hydrolyzed, when added to the emulsion.

The "reference" in this study was the 20T:0M:0G microcapsules synthetized with the pre-hydrolysis step.

Experimental results:

The microcapsules obtained through the first synthesis, that reacted at T3 during 1h30, looked immature and a poorly aggregated, when observed under optical microscope. Some core shell microcapsules could be found, however the majority seemed to be porous matrix microcapsules. The ones obtained with more reaction time at T3 seemed more mature than the previous ones, however, it was only possible to observe matrix microcapsules.

Since the objective of this study was to obtain core shell microcapsules, the characterizations were made for the first synthesis.

From the Fig. 42 it is possible to observe that, in fact, the microcapsules obtained were matrix microcapsules and not core shell, as expected. As it was already observed by optical microscope, the microcapsules are aggregated.

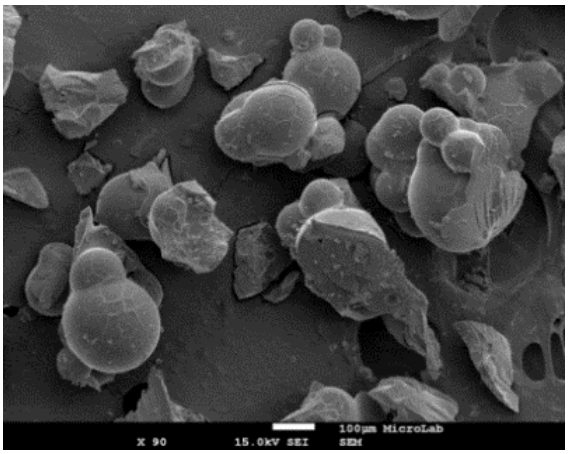


Fig. 42 – SEM of 20T:0M:0G(-hydrolysis) microcapsules, with acidic water in the emulsion

As seen in Table 17, some significant results were observed regarding the curing time of OCF, not only comparing with the foam without microcapsules but also with the foam with the reference microcapsules. This result can be due to a difference in the microcapsules porosity, due to the alteration of the hydrolysis step.

Table 17 - Curing time test results of microcapsules synthetized without the pre-hydrolysis step, and the respective references

Synthesis	Curing Rate at 10%RH				
	0h	24h	48h	67h	72h
Reference of 20T:0M:0G	-	-4	-3	-2	-
20T:0M:0G microcapsules	-	-2	0	1	-
Reference of 20T:0M:0G (-hydrolysis)	-5	-4	-2	-	-1
20T:0M:0G (-hydrolysis)	-4	0	3	-	5

The leaching in Ongrontat2500 was also studied. The test results are presented in Fig.C 1**,** appendix C. In comparison with the reference, no improvements were observed with these microcapsules. After 168 hours the Ongronat was already solid, as was observed with the reference microcapsules.

Conclusions:

Although the microcapsules obtained through this method were not core shell, as desired, some improvements in the OCF tests results were observed, when comparing with the reference ones.

For the application of these microcapsules in OCF foams, it would be necessary to previously decrease the observed leaching.

4.2.3.4. Quantity of the encapsulated compound

In this chapter, the possibility of changing the amount of glycerol to be encapsulated was studied.

The emulsion system is composed by an oil and water phase, with glycerol in the water droplets. The water is necessary for the emulsion formation, but it is not desired in the final product. So, the possibility of the emulsion to be composed of more quantity of encapsulating compound than water was studied, with the purpose of

obtain microcapsules with more encapsulated compound and to decrease the possibility of remaining water in the final product.

Experimental procedure:

In the basic procedure, the double amount, in weight, of water was added regarding the amount of glycerol. In this synthesis, the amount of each compound was exchanged, i.e. it was used the double amount of glycerol regarding the amount of water

The "reference" for this study was the microcapsules obtained through the synthesis with 20T:0M:0G, in which 15g of water and 7,5g of glycerol were used.

Experimental results:

Under optical microscope, the capsules obtained seemed larger in size than the reference ones, as well as less rigid.

From the SEM results, presented in Fig. 43 it is possible to observe that the obtained microcapsules do not have a perfect spherical shape, have big dimensions and it is possible to view some agglomeration. However, they seem to be poly-nucleated, although with small porous, which can lead to a higher amount of encapsulated glycerol.

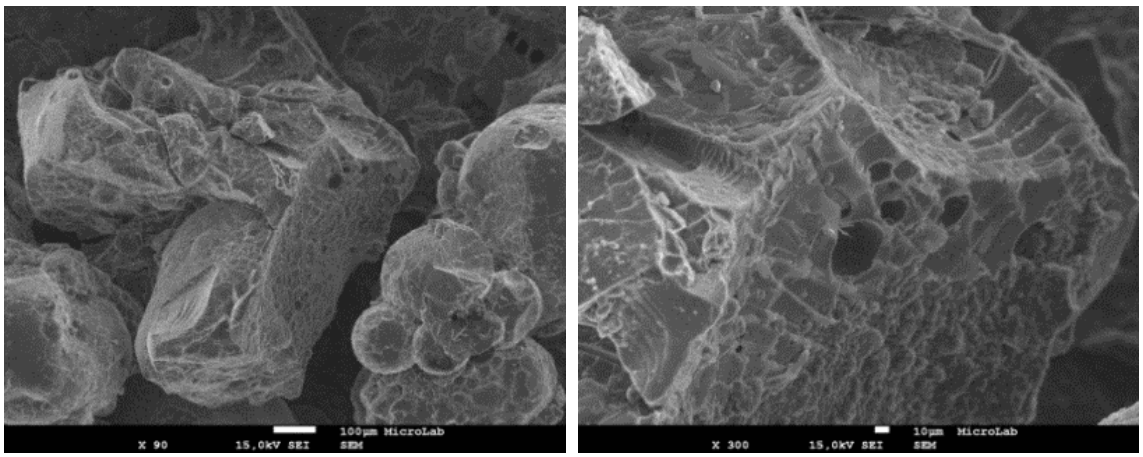


Fig. 43 – SEM of the microcapsules obtained with an increased amount of glycerol A) 90x magnification B) 300x magnification

From FTIR results, presented in appendix B, Fig.B 3, it was possible to conclude that, in comparison with the reference, the microcapsules obtained through this synthesis have an O-H band with a 3,3% more intensity and the peaks within the 1500 and 1300 cm^{-1} range, due to CH_2 and OH bending of glycerol are also slightly more intense, which reveals indeed more glycerol encapsulated in the microcapsules structure.

The results for the curing time test are presented in Table 18. The results with the microcapsules obtained in this study do not show a significant effect in the curing of the foam. In comparison, the reference microcapsules seem to have a more significant effect, which was not expected since the amount of glycerol encapsulated seem to be inferior.

Table 18- Curing time results of silica based microcapsules synthetized with an increased amount of glycerol and respective references

Synthesis	Curing Rate at 10%RH			
	24h	48h	67h	120h
Reference of 20T:0M:0G	-4	-3	-2	-
20T:0M:OG	-2	0	1	-
Reference 20T:0M:0G (+glycerol)	0	2	-	4
20T:0M:0G (+glycerol)	0	1	-	5

The results obtained for the string, tack free and cutting time were only compared with the ones obtained with the OCF foam without capsules. As seen in the Table 19 the results obtained with these microcapsules did not present a significant improvement in the curing time, when comparing with the results obtained for the OCF without capsules.

Table 19 - String, tack free and cutting time results with silica based microcapsules obtained with an increased amount of glycerol

Synthesis	String Time	Tack free Time	Cutting Time
	Seconds	Minutes	Minutes
Reference of 20T:0M:0G (+glycerol)	29	15	110
20T:0M:0G (+glycerol)	36	15	94

Viscosity studies with Ongronat® 2500 were also made. The test results are presented in Fig.C 2, appendix C. Some leaching was observed with the microcapsules synthetized in this study, however not as significant as the observed with the reference microcapsules.

Conclusions:

The results were not very conclusive. Although the O-H band was more intense than the reference, indicating that there was more glycerol encapsulated, the results obtained in the tests in OCF foams showed that these microcapsules had a less significant effect in the curing process. This might possibly be due to the fact that the microcapsules did not break during the spray

It would be important to try to decrease the size of the obtained microcapsules, in order to prevent accumulation in the nozzle after the first spray in OCF cans.

4.2.4. Changes in shell material

In this chapter, some studies regarding to alterations made to the shell's materials of some microcapsules will be described. These studies were carried out with the purpose of improving some microcapsules' characteristics, such as the mechanical resistance, the hydrophobicity of the shell and the decrease of the observed leaching.

The alterations that are described in this chapter were performed with the addition of different precursors and chemical components, presented in Table 20. In some cases, additives with desired characteristics were also added to the synthesis, which did not reacted with the precursor, but were entrapped in the silica matrix, inducing to desired alterations in the properties of shell. The last study presented in this chapter describes a post-treatment performed in microcapsules that were already subjected to 45°C heating for 48h.

Table 20 – Principal characteristics of the reagents used for changes in the shell composition

Reagents	Brand	Density (g/ml)	Viscosity (mPas) (20°C)	Purity grade (%)
EDA – Ethylenediamine	Fluka analytica	0,899	1.7	<99,5
Aminosilane	Alfa Aesar	1,010	_	90
Ongronat® 2500	BorsodChem	1,24	≈520	_

4.2.4.1. Silica/Epoxy in TEOS/GPTMS synthesis:

In this study, an attempt to produce silica based microcapsules displaying epoxy resin rich regions was conducted, in order to create hybrid capsules, as well as to add amine groups to the shell, which will be fundamental to a study presented later on this work.

The silica/epoxy microcapsules were obtained with the silanes TEOS and GPTMS and the curing agent EDA. As already mentioned in this work, the GPTMS precursor has an epoxy ring. The EDA curing agent reacts with the epoxy ring, opening it (ring opening polymerization), leading to the formation of an organic matrix, and the nitrogen molecule becomes part of the structure, as presented in Fig. 44. The structure will be more reticulated as more nitrogen groups the curing agent has.

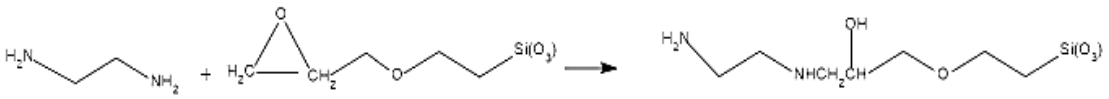


Fig. 44 – Representation of the reaction between EDA and GPTMS

Epoxy resins are used in many applications mostly because of their desirable properties: heat, solvent, moisture and chemical resistance, good mechanical and electrical properties and great adherence to many substrates.[38][39]

Experimental Procedure:

In this study, the microcapsules were synthetized with 10T:0M:10G. The ratio of EDA used was 0,55 EDA to one GPTMS molecule, since EDA has two amine groups and the GPTMS one epoxy group.

With the addition of EDA, neither high temperatures nor so much reactional time was needed, since EDA is a strong basis and, consequently, a reactional catalyst. Also, an ice bath was used while adding the hydrolysis solution to the emulsion, to which the EDA was added, and it was maintained for 30 more minutes. The ice bath was used in order to decrease the EDA reaction, since it was desired that the TEOS and GPTMS would react with each other at some extent before the EDA would react with the GPTMS silane.

The “reference” in this study will be the microcapsules 10T:0M:10G.

Experimental results:

The first synthesis (S1) was subjected to 30 minutes of reaction in an ice bath, one hour at T1 and one hour at T2. After 15 minutes reacting at T1, some polymerized material was already seen in the reactional balloon.

As seen in Fig. 45 the obtained microcapsules have a perfect spherical shape, being more similar to the ones obtained with 20T:0M:0G than to the reference ones. It can be seen in Fig. 45 a) that there is a big size distribution, 25μm to 225μm, however the microcapsules have relatively smaller sizes when compared with both silica based and the reference microcapsules. In Fig. 45 b) it is possible to observe that the microcapsules obtained are poly-nucleated microcapsules, although the pores are very small when comparing with the microcapsule’s diameter.

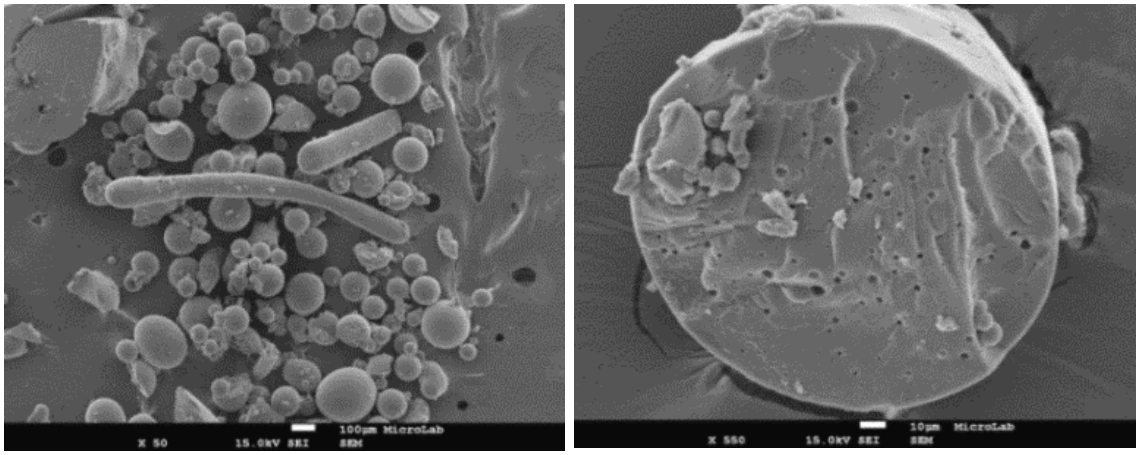


Fig. 45 – SEM images of microcapsules synthetized with EDA. a) 90x magnification b) 550x magnification

In an attempt to obtain more microcapsules, a synthesis was made, (S2), in which all the reagents used were increased to more ½ of its initial amount, i.e. 15T:0M:15G were used.

From the viscosity test results, presented in Fig.C 3, appendix C, it is possible to conclude that the microcapsules obtained through the synthesis (S1) have more leaching than the ones obtained through the synthesis (S2) and the reference. However, no significant changes were observed when comparing, for example, to the silica based ones.

From the FTIR results, presented in appendix B, Fig.B 4, it can be seen that the synthesis (S1) may have much more OH groups, from possibly more abundant encapsulated glycerol, but also those OH groups formed by ring opening polymerization (Fig. 43), which also can explain the results obtained from the viscosity tests. It is also possible to observe that, the broad O-H band of the (S1) microcapsules is shifted to shorter wavenumbers and the bands in the range of 1470 and 1430 cm^{-1} are more intense. Both these facts are an evidence of the presence of NH groups, formed by epoxy ring opening polymerization, which is a clear evidence of the successful reaction between EDA and GPTMS, forming a hybrid, silica-rich and epoxy–rich shell.

TGA analysis was also made for the synthesis (S1) microcapsules, its results are presented in Table 21 and its thermogram is presented in appendix D, Fig.D 4. It was possible to conclude that about 26,51% of the total weight of these capsules is encapsulated glycerol. When comparing with the results obtained for the reference capsules, it is possible to conclude that the ones obtained in this study have an higher percentage of encapsulated glycerol, with an increase of about 8,64%, which is accordant with the FTIR results. Regarding to water, no water loss was visible through the TGA analysis.

Table 21 - TGA results obtained with the microcapsules 10T:0M:10G(+EDA)

Onset Temperature,°C	Average Temperature,°C	% of mass lost until 300°C	% of water
137,29	215,64	26,51	≈ 0

From Table 22 it is possible to observe that there was no significant decrease in shaking rate results with the microcapsules obtained from synthesis (S1). The results obtained with these microcapsules are also similar to the reference.

From Table 23 it is possible to observe that the foam with the microcapsules obtained from synthesis (S2) does not show any improvement in the curing time results, when comparing with the reference foam. The microcapsules obtained from synthesis (S1) were the ones that had shown a more significant effect on the curing time.

Table 22 - Shaking rate test results of 10T:0M:10G and synthesis (S2) microcapsules

Synthesis	SR (Shaking Rate) (hours)			
	0h	72h	96h	120h
Foam with no MCs	5	5	3	3
Reference	5	4	3	3
Synthesis (S1)	5	4	4	2

Table 23 - Curing time test results obtained with 10T:0M:10G, synthesis (S2) and (S4) microcapsules

Synthesis	Curing Rate at 10%RH			
	24h	48h	67h	72h
Reference of 10T:0M:10G and Synhtesis (S1)	-4	-3	-2	-
10T:0M:10G microcapsules	-3	-1	-1	-
Synthesis (S1)	-2	0	0	-
Reference of Synthesis (S2)	-1	1	-	4
Synthesis (S2)	-1	1	-	4

Conclusions:

It was possible to synthetize hybrid microcapsules with EDA incorporated in the shell structure.

These microcapsules have a perfectly spherical shape, in contrast with 10:0M:10G and, in case of (S1) microcapsules, the results in the foam test showed some improvements.

Some improvement might be needed, regarding the synthesis reproducibility.

4.2.4.2. Silica/ Silicone synthesis:

The purpose of this study was to incorporate silicone (polysiloxane) in the shell, as an attempt to add Polydimethylsiloxane (PDMS) structures to the shell, since they might confer hydrophobicity to the microcapsules and, consequently, contribute to decrease the amount of superficial water, as well as the leaching, observed in some microcapsules.

Two different silicones were used for this purpose, with the trade names Baysilone and a Silopren, both from Momentive. Both silicones have OH terminated dimethylsiloxane groups, which may allow polycondensation between the silicones and the silanes, and thus covalently incorporate the silicones in the microcapsule's structure.

The Baysilone contains terminal hydroxyalkyl groups (-CH_2-OH) and the Silopren has silanol terminated dimethylsiloxanes (-Si-OH). Both the hydroxyalkyl and the silanol groups may also react with the terminal -NCO groups present in the pre-polymer inside the can.

Experimental procedure:

This study was carried out with silica based microcapsules, as an attempt to increase the shell hydrophobicity. However, since the silicones also have Si-O-Si groups, only 10g of TEOS were used.

In this study, different quantities of Baysilone were used for the microcapsules' synthesis. The amounts used are confidential, as this, G1, G2 and G3 will be used instead of the real values. The amount G2 is 1/4 of the initial Baysilone amount, G1, and G3 is 1/5.

Since the Baysilone cannot be hydrolyzed and the silopren already has Si-OH terminal groups, the silicones were not subjected to a previous step of agitation in acidic water. However, they were added to the pre-hydrolysis solution and left in agitation with the already hydrolyzed TEOS in an attempt to homogenize the silanes with the silicones. It was necessary to alter the period of time at which the reactions were subjected to heating at T3, since all the syntheses were left to react during the night under the referred temperature.

Experimental results:

- **Baysilone:**

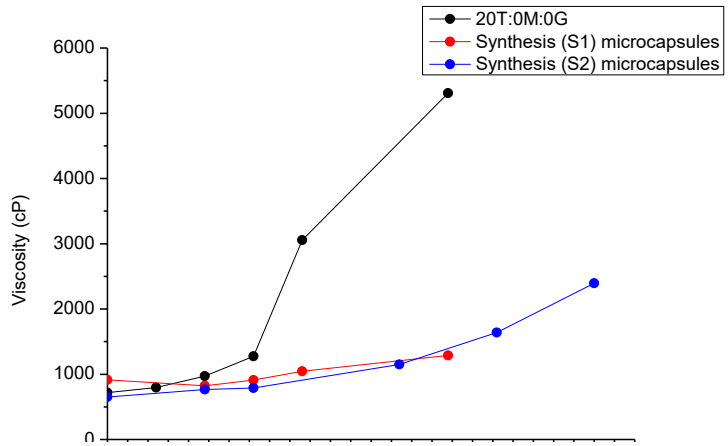
The first synthesis was made with G1 as the Basylone amount; however there was no microcapsules formation.

The second synthesis (S1) was made with G2 as the Baysilone amount. Through this synthesis, the obtain microcapsules were very gelatinous, possibly because more

reaction time was needed or too much silicone was used. Since the synthesis was left to react during the night, which already is a long period of time for the synthesis to occur, the amount of silicone used was decreased. After heat treatment (drying), the microcapsules were very rigid and agglomerated.

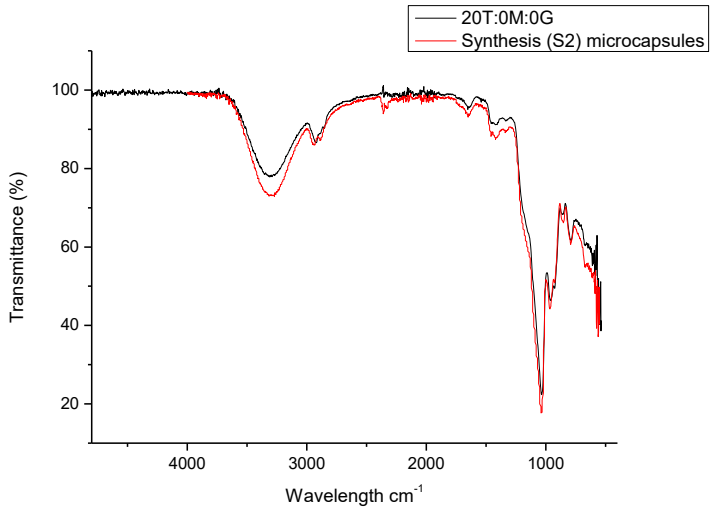
Thus, a third synthesis (S2) was made, with G3 as the Baysilone amount. The microcapsules obtained were a little less gelatinous, however, after being subjected to the oven were also very aggregated.

The Graphic 9 presents the leaching results. As it is possible to observe, it seems that there was a significant decrease in the microcapsules' leaching with the presence of Baysilone in the shell, as it was desired, basically due to the hydrophobicity imparted by the presence of PDMS in the shell structure.



Graphic 9 – Leaching test results for silica based and silica/Baysilone microcapsules

Graphic 10 presents the FTIR results for the reference microcapsules, as well as for the ones obtained through the synthesis (S2). As it can be seen, there was a slight increase in the intensity of the O-H band and of those peaks ascribed to glycerol at ca. 1300-1100 cm^{-1}, in the case of the microcapsules prepared with silicone. This increase must be due to more encapsulated glycerol, since the microcapsules with Baysilone are supposedly more hydrophobic and, thus, there is a lower tendency for the water to accumulate at the microcapsules surface. However more characterization technics would be needed to guarantee it.



Graphic 10 – FTIR results of silica based and Synthesis (S2) microcapsules

- **Silopren:**

Two syntheses with Silopren were made. In both synthesis the amount of Silopren used was G3, which is the same amount referred in the case of Baysilone. The first one, synthesis (S3) was left to react during the night at T3. The microcapsules obtained through this synthesis were not gelatinous, as the ones obtained with Baysilone.

Since the microcapsules obtained through synthesis (S3) did not seem gelatinous, in the second synthesis (S4) the reaction was stopped after 4h at T3, in an attempt to decrease the synthesis time needed. The result was identical to the one obtained in synthesis (S3).

Fig. 46, presents the SEM results of the microcapsules obtained through the synthesis (S4). As it can be seen, the obtained microcapsules are very different from the reference ones. Its shape is irregular, instead of perfectly spherical, and the surface seems rough, not as smooth as the reference microcapsules' surface.

From the cross section of a broke microcapsule it is possible to observe that it has two minimal cores in the center, however too small in comparison with the microcapsule diameter.

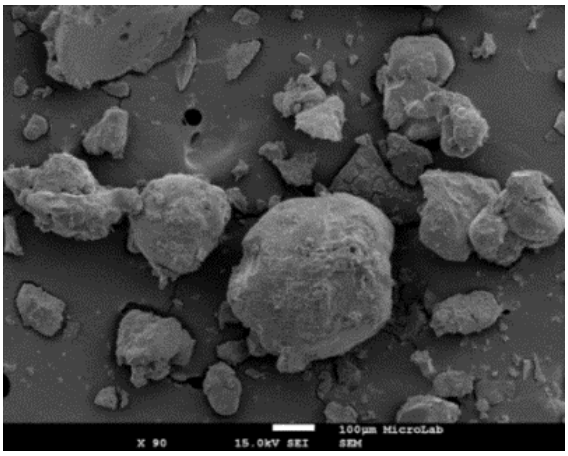


Fig. 46 – SEM image of the microcapsules obtained from synthesis (S4)

The leaching test results are presented in Fig.C 4, appendix C. As it can be seen, distinguish results were obtained, from synthesis (S3) and synthesis (S4). An improvement was observed in the case of the microcapsules obtained from the synthesis (S3), while, in the case of synthesis (S4) microcapsules, more leaching was observed, when comparing with the reference microcapsules. This difference might be due to the different reaction times at which the microcapsules were subjected.

From FTIR results, presented in appendix B, Fig.B 5, it is possible to observe that the microcapsules with Silopren have a more intense O-H band than the silica-based ones, which was also observed in the microcapsules with Baysilone. The increase in the O-H band intensity might be due to more glycerol encapsulated, in comparison with the reference microcapsules. Since, due to the hydrophobicity conferred by the silicones, an increase of the superficial water was not expected.

From Table 24 and Table 25 it is possible to conclude that, the results obtained from the foams with the capsules do not show any improvements when comparing to the reference foams without capsules. Since the microcapsules might have a higher amount of encapsulated glycerol, as was observed from the FTIR spectra, these results may be due to the fact the microcapsules might not breaking during the spray process.

Table 24 – Curing time test results for the microcapsules synthetized with Silopren, as well as for silica based microcapsules

Synthesis	Curing Rate at 10%RH				
	24h	48h	67h	72h	120h
Reference of Synhtesis (S3)	-1	1	-	4	-
Synthesis (S3)	0	2	-	5	-
Reference of synthesis (S4)	0	2	-	-	4
Synthesis (S4)	-2	0	-	-	3
Reference of 20T:0M:0G microcapsules	-4	-3	-2	-	-
20T:0M:0G microcapsules	-2	0	1	-	-

Table 25 - String, tack and cutting time test results for the microcapsules synthetized with Silopren

Synthesis	String Time	Tack free Time	Cutting Time
	Seconds	Minutes	Minutes
Reference of Synthesis (S3)	45	19	97
Synthesis (S3)	28	20	102
Reference of synthesis (S4)	29	15	110
Synthesis (S4)	40	15	115

Conclusions:

In the case of the microcapsules with Baysilone, it was observed an improvement in the leaching test results, indicating a possible increase in the hydrophobicity of the shell.

For the microcapsules with Silopren, it was not possible to conclude about their hydrophobicity, since opposite results were obtained in the leaching tests with these microcapsules.

Also, although there might be more encapsulated compound, no effect was observed in the curing of the OCF foams, indicating that the microcapsules might not be breaking during the spray process.

4.2.4.3. Cork addition:

The purpose of this study was to incorporate cork powder in the microcapsules' shell structure, forming a composite material. Indeed, the cork powder will not react with

the silanes used in the synthesis; instead it will be entrapped in the silica matrix. The principal aim of this study is to provide some of the cork's desirable characteristics to the microcapsules, such as: more elasticity, in an attempt to produce less fragile microcapsules; and impermeability to water, which is desired as a way to decrease the superficial water and the leaching of the encapsulated glycerol.[41]

Since Portugal is the major cork producer, with about 55% of the cork global production, the use of this sub-product for the microcapsule synthesis could also be interesting, as a way to give use to a sub-product of a major national industry. [42]

This study was made with the silica based microcapsules, since those are the ones that need more shell elasticity, as well as some hydrophobicity. Afterwards, the cork was also applied to silica/epoxy microcapsules, in continuity to the referred microcapsules study.

- **Silica based microcapsules:**

Experimental procedure:

Two syntheses were made, with C1 and C2 amounts of cork, in which C1 is a higher value than C2. The exact amount of cork used for the synthesis is confidential. The cork was added to the hydrolysis solution, and left under stirring for 15 minutes, in order to obtain a good homogenization.

Two more syntheses were made, with the water used for the hydrolysis in the emulsion system and with C3 as the cork amount, in which C3 is inferior value than C2. The pre-hydrolysis was not made.

The "reference", in this study, is the 20T:0M:0G microcapsules, without the cork.

Experimental results:

The first synthesis was made with C1 as the cork amount, synthesis (S1). The microcapsules obtained through this synthesis were gelatinous and aggregated, as seen in Fig. 47.

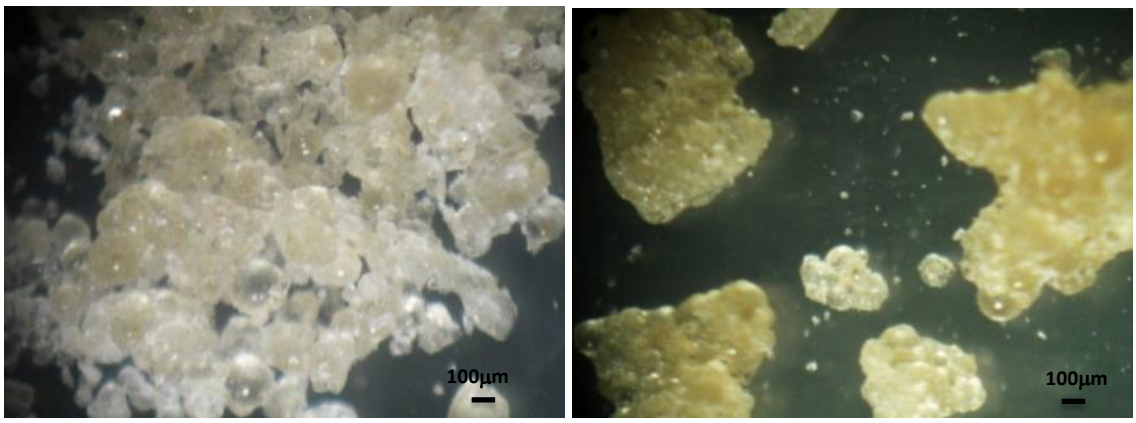


Fig. 47 – Microcapsules obtained in synthesis (S1), under optical microscope

Therefore, the amount of cork used was decreased to C2, synthesis (S2). However, the resulting microcapsules were identical. Two more syntheses were made, without the pre-hydrolysis step and decreasing the amount of cork used to C3. In the synthesis (S3), the microcapsules obtained were loose and not as rigid as the previous ones. As seen in Fig. 48 the microcapsules have a more spherical shape and are less aggregated than the ones obtained from synthesis (S1). From Fig. 48 b) it is possible to observe core shell microcapsules.

An attempt to reproduce the synthesis (S3) was conducted, however without a satisfactory result, under optical microscope the obtained microcapsules seemed identical to the ones obtained from the syntheses (S1) and (S2).

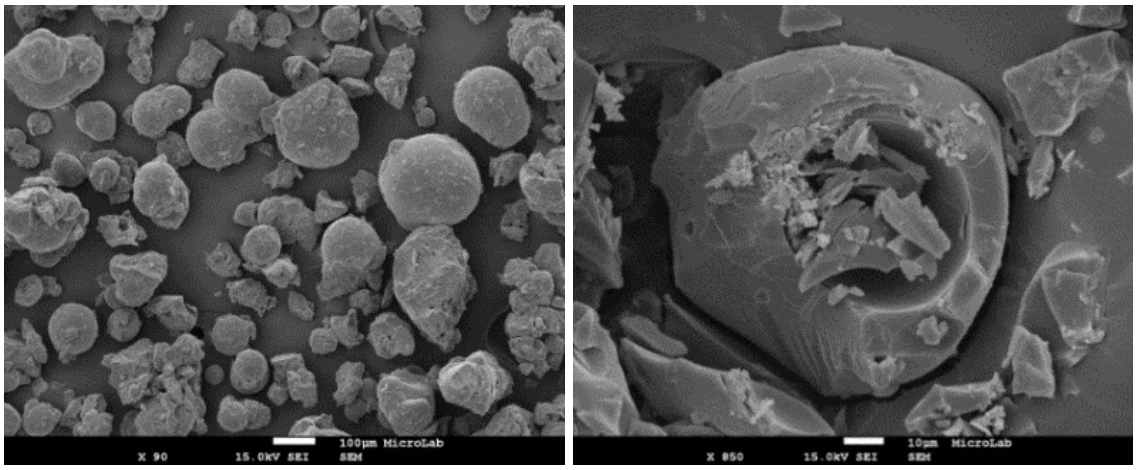


Fig. 48 – SEM images of the microcapsules obtained from Synthesis (S3) microcapsules. a) 90x magnification b) 850x magnification.

Viscosity tests were made to the microcapsules obtained from the synthesis (S1), (S2) and (S4). The test results are presented in Fig.C 5, appendix C. It is possible to conclude that, except for the ones obtained from the synthesis (S1), the microcapsules present less leaching than the reference ones. While the Ongronat® 2500 reached the 5000 cP value after 168h with the reference microcapsules, it was necessary more than 300h to reach that value with the microcapsules obtained from synthesis (S2) and (S4).

FTIR tests were made for the microcapsules obtained from synthesis (S1) and (S2). From the obtained results, presented in appendix B, Fig.B 6, it is possible to observe that the O-H band from microcapsules with cork have approximately the same intensity as the one obtained with the reference, which means that the encapsulation should be identical in both cases.

The FTIR results were also compared with the ones obtained with the cork powder. The characteristically cork FTIR bands are at 1736cm^{-1}, from ester groups of suberin, and at 2920 cm^{-1} from C-H stretching of suberin aliphatic chains[43][44]. From the FTIR results it is possible to conclude that there are no bands visible at 1736cm^{-1}. The band presented at 2920cm^{-1}, also visible for silica based microcapsules since they also have

–CH bondings, is more intense for the microcapsules with cork, which might be indicative of the presence of the cork in microcapsules.

TGA characterization was made for the syntheses (S3) and (S4) microcapsules, the results are presented in Table 26 and the respective thermograms are presented in the appendix D, Fig.D 5 and Fig.D 6. It is possible to conclude that the synthesis (S3) is the one with the higher percentage in mass of encapsulated glycerol, with a difference of 7,17%. Regarding water presence in the microcapsules, it was not possible to observe any loss through TGA analysis for the synthesis (S3) and (S4).

Table 26 - TGA results of the microcapsules obtained through the synthesis (S3) and (S4)

Synthesis	Onset Temperature,°C	Average Temperature,°C	% of mass lost until 300°C	% of water
S3	149	216	42,17	≈0
S4	162,94	235,2	35,543	≈0

As it is possible to confirm from the curing time results, presented at Table 27, only the microcapsules obtained from the synthesis (S3) had a significant effect in the foam's curing time, showing a better result than the reference microcapsules. These results are in accordance to the ones obtained with the TGA analysis, through which it was observed that the synthesis (S3) had the highest % in mass of encapsulated glycerol. Independently from the MCs´ quality and glycerol encapsulated, it should be noted that if the size of the microcapsules is too small (smaller than 100µm) they will not be able to burst by pressure drop or simply by turbulence when sprayed out from the can.

Table 27 - Curing time test results with the synthesis (S2), (S3) and (S4) microcapsules and respective references

Synthesis	Curing Rate at 10%RH				
	24h	48h	67h	72h	120h
Reference of Synhtesis (S2)	0	2	-	-	4
Synthesis (S2)	-2	-1	-	-	3
Reference of synthesis (S3)	-5	-5	-	-2	-
Synthesis (S3)	-5	-3	-	2	-
Reference for the synthesis (S4)	-4	-3	-	-	-
Synthesis (S4)	-4	-3	-	-	-
Reference of 20T:0M:0G microcapsules	-4	-3	-2	-	-
20T:0M:0G microcapsules	-2	0	1	-	-

Table 28 presents the results obtained for the string, tack and cutting time tests. As it is possible to confirm, there are no significate improvements in the results with the microcapsules obtained from this synthesis.

Table 28 - String, tack and cutting time results with the synthesis (S1), (S2) and (S3) microcapsules

Synthesis	String Time	Tack free Time	Cutting Time
	Seconds	Minutes	Minutes
Reference for synthesis (S2)	29	15	110
Synthesis (S2)	16	15	118
Reference for synthesis (S3)	140	28	111
Synthesis (S3)	75	27	-
Reference for synthesis (S4)	88	31	118
Synthesis (S4)	135	22	-

Conclusions:

It was possible to synthesize 20T:0M:0G(+cork), although the synthesis reproducibility has to be improved.

The microcapsules obtained in this study contain approximately the same amount of encapsulated glycerol than the silica based ones, with the benefit of a lower leaching.

However, from all the synthesis made, only one led to the formation of microcapsules that contributed to a significate improvement in the foam curing times.

- **Silica/Epoxy microcapsules:**

Experimental procedure:

In these syntheses, the pre-hydrolysis solution was added to a reactional balloon in an ice bath. After 30minutes reacting at low temperature, they were left for 1h at T1 and posteriorly for 2h at T2. The syntheses did not react at T3.

The amount of EDA used in the synthesis was 1,33g, which is the same amount used for the silica/Epoxy microcapsules synthesis, presented in on chapter 5.2.4.1 .

The “reference”, in this study, are the 10T:OM:10G (+EDA) microcapsules, without cork.

Experimental results:

Initially, two types of materials were obtained, as seen in Fig. 49. Small spherical shaped microcapsules of pale yellow and big amorphous shaped spheres of darker yellow were visible, the latter being the most abundant.

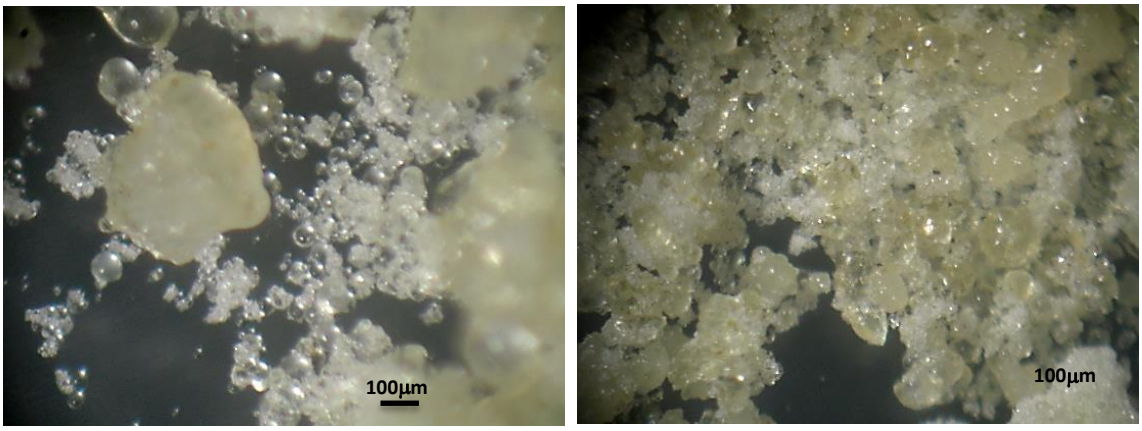


Fig. 49- Silica/Epoxy microcapsules obtained with 0,07g of cork.

In the previous syntheses, the EDA was added to the water phase of the emulsion system, as in the study presented in 5.2.4.1. For the next syntheses, the EDA was only added after the silanes were already in the reaction balloon, while in an ice bath. Thus, mostly small microcapsules were obtained, as seen in Fig. 50.

Fig. 50- Silica/Epoxy microcapsules obtained with C3 as the amount of cork, under optical microscope

Three syntheses were made (S1), (S2) and (S3) through the last referred method. However, some differences were observed between the obtained microcapsules; the color of the capsules varied as well as the amount of big spheres, although it was always substantially inferior when comparing to the first synthesis.

Fig. 51 presents the SEM results for the microcapsules presented in Fig. 50. As it can be seen, they have a perfectly spherical shape and a smooth surface, similar to the reference microcapsules. However, instead of poly-nucleated, the microcapsules seem to be core shell, although with a small core. The microcapsules obtained through this synthesis are the smallest microcapsules presented so far, with some having diameters with less than 10μm and the larger ones having about 20μm. In comparison, the reference ones are significantly larger, with the smallest microcapsules having around 50μm.

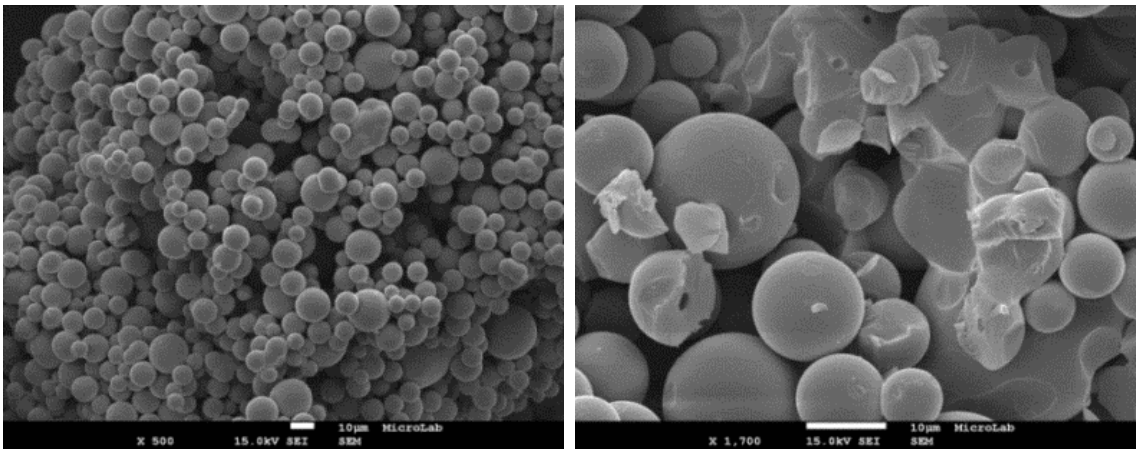


Fig. 51 – SEM images of 10T:0M:10G (+EDA + cork) microcapsules. a) 500x magnification b) 1700x magnification

The leaching test results are presented in Fig.C 6, appendix C. From this test, it was observed that, contrariwise to what was expected, the microcapsules synthetized with cork seem to have more leaching than the reference ones.

Through the comparison of the FTIR results, presented in appendix B, Fig.B 7, it is possible to conclude that the intensity of O-H band of the microcapsules obtained through the synthesis (S3) is identical to the one observed with the reference microcapsules. The intensity of the O-H band of the microcapsules obtained through

the synthesis (S1) is significantly inferior. Comparing these microcapsules FTIR with the one obtained with cork, it is not possible to draw any conclusions regarding its presence. Although the band located at 2920cm^{-1}, due to the presence of C-H strength and to suberin aliphatic chains is present in the microcapsules FTIR, it has the same intensity for the microcapsules with and without cork. Also, the characteristic cork band, located at 1736cm^{-1}, due to the ester groups of suberin, is not visible.

As seen in Table 29and Table 30 there were no improvements in the curing time of the foams with synthesis (S1) and (S3) microcapsules, as well as for the string, tack free and cutting time tests. These may be due to a lack of capsules breaking during the spray. Indeed, their size is possibly too small to enable them to burst.

Table 29- Curing time test results of 10T:0M:10G(+EDA), synthesis (S1) and Synthesis (S3) microcapsules, as well as the respecting references.

Synthesis	Curing Rate at 10%RH				
	24h	48h	67h	72h	120h
Reference of 10T:0M:10G(+EDA) microcapsules	-4	-3	-2	-	-
10T:0M:10G(+EDA) microcapsules	-2	0	0	-	-
Reference of synthesis (S1)	-1	1	-	4	-
Synthesis (S1)	-3	-1	-	2	-
Reference for the synthesis (S3)	0	2	-	-	4
Synthesis (S3)	-1	1	-	-	4

Table 30 - String, tack and cutting time results of 10T:0M:10G(+EDA) microcapsules, synthesis (S1) and (S2) microcapsules, as well as the respective references.

Synthesis	String Time	Tack free Time	Cutting Time
	Seconds	Minutes	Minutes
Reference for synthesis (S1)	45	19	97
Synthesis (S1)	42	23	90
Reference for synthesis (S3)	29	15	110
Synthesis (S3)	36	15	97

Conclusions:

It was possible to synthetize 10T:0M:10G (+EDA+cork) microcapsules.

The microcapsules have a perfectly spherical shape and are not aggregated.

The amount of encapsulated glycerol seems to be identical to the one observed in the reference microcapsules.

However, contrarily to what was expected, these microcapsules had more leaching and, through the results obtained in the foam tests, it was possible to conclude that they had no significate effect in the curing process of the foams.

4.2.4.4. Production of a second shell of amino-functional silica

In this study, a second shell with an aminosilane, was produced for the 20T:0M:0G microcapsules. The principal aim of this study was to produce a shell with amino groups that could be posteriorly treated with Ongronat® 2500 in order to obtain a polyurea shell. Also, it was hoped that, with the second shell, the silica based microcapsules would be more resistant and it could lead to a decrease in the leaching observed for the inorganic silica based microcapsules.

Experimental procedure:

Two different studies were made. In the first study, the pre-hydrolysis step was not made, instead the water usually used for this step was applied in the emulsion system formation. In the second, the microcapsules were synthetized with two surfactants. In both cases, the aminosilane was not pre-hydrolyzed. In both studies, the aminosilane was added to the reactional balloon at the end of the synthesis, when it was already reacting at T3 for almost one hour. After the addition of the aminosilane, it was left to react for some minutes before the synthesis was stopped.

Experimental results:

- Synthesis conducted without the pre-hydrolysis step

Fig. 52 presents the SEM results for the 20T:0M:0G:10A microcapsules. It is possible to observe that the microcapsules have a perfectly spherical shape and a smooth surface, as it was observed in silica base ones. The microcapsules seem to be matrix, as observable in Fig. 52 b), and not core shell or poly-nucleated.

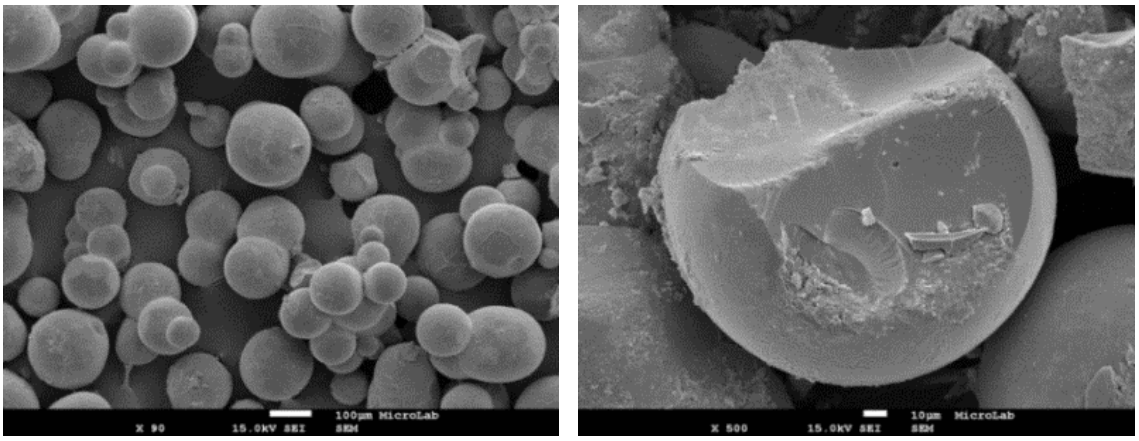


Fig. 52 – SEM results of silica based microcapsules with a double amino-functional silica shell a) 90x magnification b)500x magnification.

Table 31 presents the principal results obtained through TGA analysis, the respective TGA thermogram is presents in appendix D, Fig.D 7. As it can be seen, about 24,24% of these microcapsules' weight is due to encapsulated glycerol. When comparing this result with the ones obtained for the silica based microcapsules with cork, it is possible to conclude that the microcapsules with the amino-functional silica double shell have a lesser percentage in weight of encapsulated glycerol, with a difference of 18,46% and 11,29%, depending on the synthesis.

Table 31 – TGA analysis of the silica based microcapsules with a double amino-functional silica shell, with acidified water in the emulsion.

Onset Temperature,°C	Average Temperature,°C	% of mass lost until 300°C	% of water
128	206	24,25	≈0

From Table 32, it is possible to conclude that the microcapsules obtained in this study positively contributed for the curing of the foams, with a result in the curing time test not very different from the ones obtained with the 20T:0M:0G microcapsules.

Table 32 – Curing time test results for the microcapsules obtained through the synthesis (S1) and (S2), as well as the respective references.

Synthesis	Curing Rate at 10%RH			
	0h	24h	48h	67h
Reference of Synthesis (S1)	-5	-5	-4	-
Synthesis (S1)	-5	-3	-2	-
Reference of 20T:0M:0G microcapsules	-	-4	-3	-2
20T:0M.0G microcapsules	-	-2	0	1

Table 33 presents the curing time test results with the microcapsules obtained in this study when sprayed with different nozzles. It is possible to observe that, with the use of the nozzle12, the results for the curing time test are significantly better. This might be an indication that not all of the microcapsules break during the spray process without the use of a nozzle.

Table 33 – Curing time test results with synthesis (S2) microcapsules, when the foam is sprayed with nozzles

Synthesis	Curing Rate at 10%RH		
	0h	24h	48h
Nozzle 11	-	-3	-2
Nozzle 12	-	-2	0
Nozzle 9	-	-3	-3

Table 34 presents the string and tack-free time results. As it can be seen, there were no major improvements with the microcapsules obtained in this study. However, as it can be seen from Table 35, significant improvements were achieved with the use of the

nozzle 11 and 12. With the nozzle 11, a decrease in 50 minutes was observed for the cutting time and, for the nozzle 12, a decrease of 40 minutes was registered. This corresponds to a decrease of the time needed for the cutting time of 45,5% and 36,37% respectively. These results indicate that the microcapsules might not be breaking during the spraying process.

Table 34 – String, tack and cutting time results obtained with the synthesis (S1) and (S2) microcapsules

Synthesis	String Time	Tack free Time
	Seconds	Minutes
Reference	110	36
Synthesis (S1)	80	20
Synthesis (S2)	80	23

Table 35 – String, tack and cutting time results obtained with synthesis (S2), when the foam is sprayed with nozzle

Synthesis	String Time	Tack free Time	Cutting Time
	Seconds	Minutes	Minutes
Nozzle 11	73	23	60
Nozzle 12	31	24	70
Nozzle 9	50	45	84
Nozzle 6b	35	29	80

- **Synthesis with two surfactant**

Two microcapsules syntheses were conducted, using two surfactants, named synthesis (S1) and (S2). Synthesis (S2) is a reproduction of synthesis (S1). This was aimed at increasing the amount of encapsulated glycerol.

From the SEM results, presented in Fig. 53, it is possible to observe that the microcapsules obtained in this study neither have a perfect spherical shape nor a smooth surface. Also, these microcapsules appear to be poly-nucleated, instead of matrix, as the previous ones, which is a desirable characteristic.

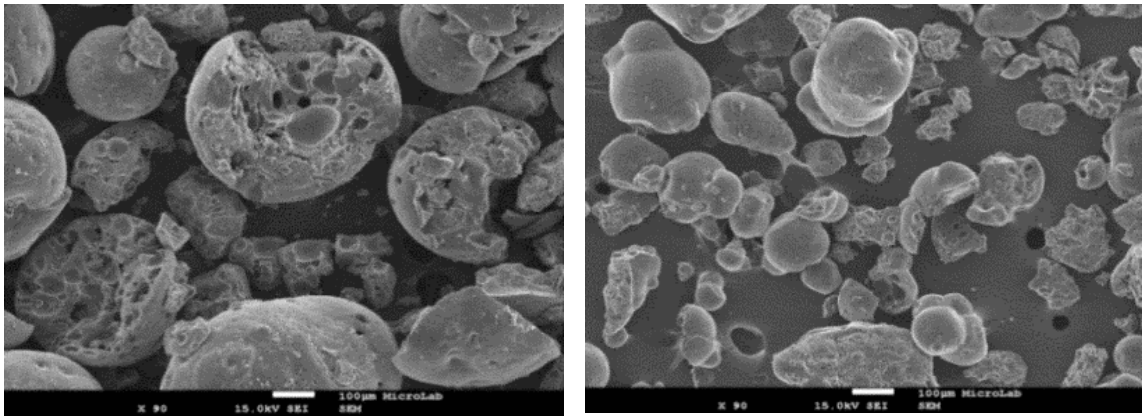


Fig. 53 – SEM images with 90x magnification of the microcapsules obtained through the two syntheses

From the FTIR results, presented in appendix B, Fig.B 8, it is possible to observe that the O-H band of the microcapsules obtained through both synthesis, (S1) and (S2), had a lower intensity than the 20T:0M:0G microcapsules.

The primary and secondary amines stretch band is located in the same region of the O-H stretch, but more shifted to shorter wavenumbers. However, for the microcapsules obtained through the synthesis (S1), and (S2) it is visible a band at around 1580cm^{-1} and 1600cm^{-1}, respectively, both not present in the FTIR spectra of silica based microcapsules. Since the N-H bend band is located between 1550cm^{-1} and 1650cm^{-1}, the presence of the referred bands in these syntheses microcapsules FTIR might be due to the presence of N-H groups, confirming the presence of the amino-functional silica.

From the leaching test results, presented in Fig.C 7, it is possible to conclude that the microcapsules obtained in this study show a significant improvement in the leaching, when comparing with the results obtained with the silica based ones. After 168h, i.e. 7 days, the Ongronat® 2500 with the microcapsules obtained through the syntheses (S1) and (S2) still had a low viscosity value of 915cP and 990cP, respectively. In comparison, after only 168h, the Ongronat® 2500 with the silica based microcapsules had already a viscosity value superior to 5000cP. However, the observed improvement might be due to a less amount of encapsulated glycerol, as seen from the FTIR results.

Conclusions:

It was possible to synthetize poly-nucleated silica based microcapsules with a second amino-functional silica shell, using two surfactants.

These microcapsules show less leaching than the silica based ones; however they also seem to have less glycerol encapsulated. Thereby, for a future application, it would be interesting to try to increase the amount of glycerol encapsulated in these microcapsules.

4.2.4.5. Post-treatment of amino-functional silica second shell microcapsules

The aim of this study was to produce microcapsules with a second shell of polyurea, since it is an hydrophobic component and thus might lead to a decrease of the observed leaching in silica based microcapsules.

The polyurea shell is a result of the reaction of isocyanate with amino terminated compounds, as seen in Fig. 54. Thereby, in this study, 20T:0M:0G:0A microcapsules were used. The referred microcapsules were left to react with Ongronat® 2500, an oligomeric, Methylene diphenyl diisocyanate, MDI with its principal characteristics presented in Table 36.

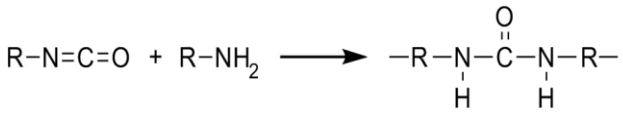


Fig. 54 – Urea linkage formation

Table 36- Ongronat®2500 principal characteristics

Reagents	Brand	Density (g/ml)	Purity grade (%)
Ongronat®2500	BorsodChem	1.24	_

Experimental procedure:

This study was made with the 20T:0M:0G:10A microcapsules, synthetized with two surfactants. The microcapsules were left to react in a diluted Ongronat®2500 solution, in a reactional balloon with magnetic stirring, under heating at 65°C. Three different post-treatments were made with different reactional times: 15 minutes, 30 minutes and 1 hour.

Experimental results:

From Fig. 55 it is possible to compare the amino-functional silica shell surface, in a) with the surface composed by polyurea in b). As it can be seen, the surface of the microcapsules with amino-functional silica shell seems to be smoother than the one that suffered a post-treatment with Ongronat® 2500.

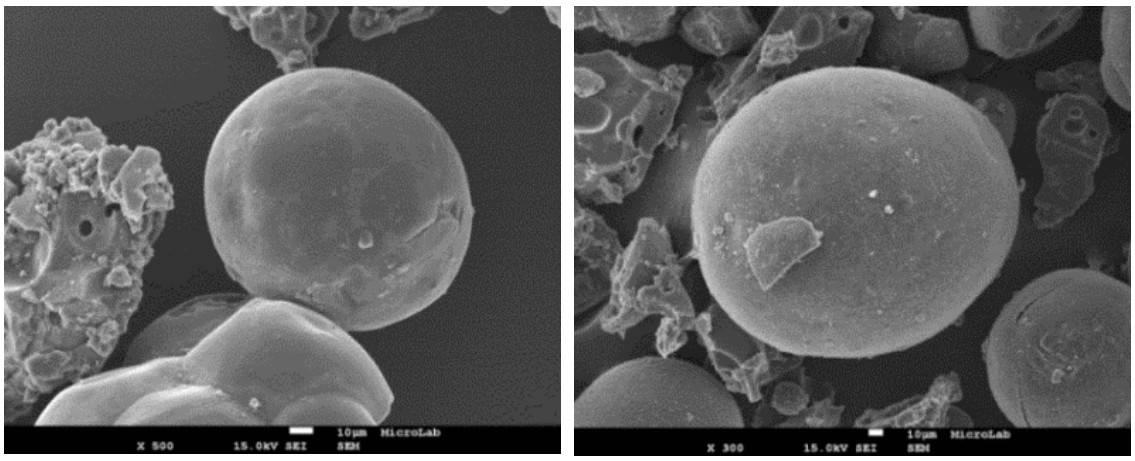


Fig. 55 – a) 20T:0M:0G:10A shell; 500x magnification. b) 20T.0M:0G:10A(+Ongronat®2500)

From the FTIR results, presented in appendix B, Fig.B 9, it is possible to observe that the intensity of the O-H band is identical for the microcapsules with amino-functional silica and with polyurea shell. In the FTIR spectra of the microcapsules that were subjected to the post-treatment, three bands that are not visible in the 20T:0M:0G:10A microcapsules FTIR are observable, located at around 1600cm^{-1}, 1536cm^{-1} and

1518cm^{1}. It might be due to the presence of nitro compounds, confirming the presence of the polyurea and, thus, the success of the post-treatment.

The leaching test results are presented in Fig.C 8, appendix C. As it can be seen, it is possible to conclude that the results obtained with the 20T:0M:0G:10A(+ongronat®2500) microcapsules for the three post-treatments are identical to the ones obtained for the amino-functional silica shell microcapsules.

It is possible to observe, from the Table 37, that the microcapsules with the polyurea shell led to a decrease, although not very significate, in the time needed for the foam to reach the cutting time, with a decrease of 20minutes from the reference foam.

Table 37 - String and tack free and cutting time results with the polyuria microcapsules

Synthesis	String Time	Tack free Time	Cutting Time
	Seconds	Minutes	Minutes
Reference	105	11	75
20T:0M:0G:10A(+ongronat®2500) (60min.)	97	11	53

Regarding the results obtained for the curing time test, presented in Table 38, no improvements were observed with the presence the microcapsules in the foam.

Table 38 - Curing time test results with the polyuria microcapsules

Synthesis	Curing Rate at 10%RH							
	0h	24h	48h	72h	168h	192h	216h	240h
Reference	-4	-3	-3	1	2	4	5	5
20T:0M:0G:10A(+ongronat®2500)	-4	-4	-4	-2	0	3	4	5

Conclusions:

It was possible to synthetize silica based microcapsules with a polyurea second shell.

There was a decrease in the leaching with these microcapsules in comparison with the silica based ones.

The foam tests showed that these microcapsules do not significantly contribute for the curing process of the foams. Possibly, more encapsulated glycerol was needed, since the FTIR results showed that the O-H band of these microcapsules have a lesser intensity than the one obtained for the silica based ones.

4.2.4.6. Encapsulation of different compounds - glycerol, diethylene glycol, glycerol carbonate

In this study, two other compounds with OH groups were encapsulated: glycerol carbonate, and diethylene glycol. The principal characteristics of the two compounds are presented in Table 39, and the molecule representation in Fig. 56.

Table 39 – Reagent characteristics

Reagents	Brand	Density (g/ml)	Purity grade (%)	Boiling Point (°C)
Glycerol	VWR Chemicals	1.261	87	290
Glycerol Carbonate	UBE chemical Europe, S.A.	1.4	_	110 - 115
Diethylene Glycol	Sigma Aldrich	_	99	244-245

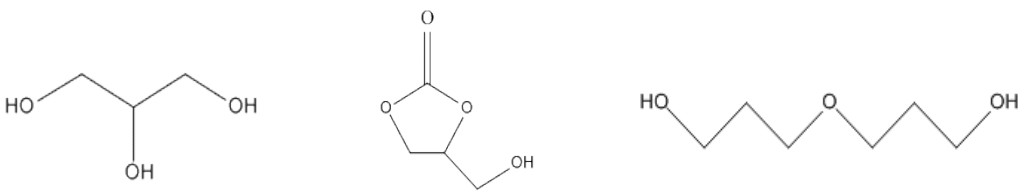


Fig. 56 – a) Glycerol molecule b) Glycerol Carbonate molecule c) Dyethilene Glycol molecule

The glycerol carbonate is a glycerol derived compound that has gain much interest in the past years, since it has a versatile reactivity, due to its hydroxyl and 2-oxo-1,3-dioxolane group. Also, the glycerol carbonate production appears as a way to valorize wasted glycerol, which is becoming widely available and suffered a significant devaluation in the past years, mainly due to biodiesel production. [45] Glycerol carbonate has been used as solvent, chemical intermediate, surfactant, among others applications. [45]

Dyethilene glycol, DEG, is a widely used solvent, being also used as a chemical intermediate, and surfactant, in the manufacture of plasticizers, polyurethanes and polyester resins, among others applications. [46]

Experimental procedure:

- **Glycerol carbonate:**

This study was performed with 10T:0M:10G microcapsules.

Since the glycerol carbonate has the boiling point at 110 - 115°C [45], the reactional temperature could not be elevated to T3, in order to avoid the evaporation of this compound. Thus, microcapsules were synthetized with lower reactional temperatures, consequently more reactional time was needed. In these syntheses, the amount, in mass, of the encapsulated compound was maintained.

- **Diethylene glycol:**

The encapsulation of diethylene glycol was made with the 10T:0M:10G microcapsules. Two different studies were made, one with only diethylene glycol as the compound to be encapsulated and another with 50% glycerol, in mass, and 50% diethylene glycol. Also, some adjustments were made in the amount of reactional time needed for the microcapsules synthesis to be completed.

Experimental results:

- **Glycerol carbonate:**

Microcapsules with 10T:0M:10G(+glycerol carbonate) were synthetized, since it seems that GPTMS do not need so much polycondensation time as the MTES. With this synthesis, it was only necessary 1 hour at T3 to obtain mature microcapsules.

As it can be seen in Fig. 57 despite of being a little aggregated, these microcapsules are the best obtained so far with 10T:0M:10G, with some spheres being distinguishable from the agglomerates.

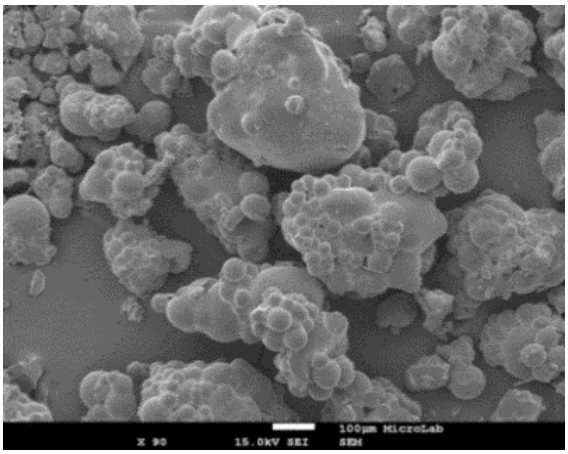


Fig. 57 – SEM of 10T:0M:10G(+glycerol carbonate) microcapsules, with 90x magnification.

From the FTIR results, presented in appendix B, Fig.B 10, is possible to observe that the O-H band is slightly more intense in the case of glycerol carbonate microcapsules than it is for the 10T:0M:10G microcapsules. Since the glycerol molecule has more O-H groups than the glycerol carbonate, the obtained results indicate that the amount of encapsulated compound was significantly higher in the case of glycerol carbonate synthesis. Also, a band is visible around 1772cm^{-1}, that might be due to the C=O group, confirming the encapsulation of the referred compound.

Regarding the leaching tests, the results, presented in Fig.C 9, appendix C, showed an increase in the leaching for the microcapsules synthetized with glycerol carbonate.

Regarding the tests made with the microcapsules in the foams, the results were not very conclusive. As seen in the Table 40, the microcapsules with glycerol had shown a more significant effect in the string, tack-free and cutting time test, than the ones with glycerol carbonate.

Table 40 – String, tack and cutting time results obtained for the 10gTEOS 10gGPTMS microcapsules with glycerol, glycerol carbonate, and respective references

Synthesis	String Time	Tack free Time	Cutting Time
	Seconds	Minutes	Minutes
Reference of 10T:0M:10G(+glycerol carbonate)	180	35	140
10T:0M:10G(+glycerol carbonate) microcapsules	60	25	105
Reference of 10T:0M:10G	120	24	150
10T:0M:10G microcapsules	60	24	90

However, the curing time test results, presented in the Table 41, indicate that, at least until 48h after the spraying, both the microcapsules hade the same effect in the curing of the foams.

Table 41 – Curing time results obtained with the 10gTEOS 10gGPTMS microcapsules with glycerol and glycerol carbonate, and respective references

Synthesis	Curing Rate at 10%RH						
	0h	24h	48h	67h	72h	144h	168h
Reference of 10T:0M:10G(+glycerol carbonate)	-4	-3	-2	-	0	3	5
10T:0M:10G(+glycerol carbonate) microcapsules	-4	-2	0	-	2	5	5
Reference of 10T:0M:10G	-	-4	-3	-2	-	-	-
10T:0M:10G microcapsules	-	-3	-1	-1	-	-	-

- **Diethylene glycol:**

Initially this study was made with 100% of diethylene glycol as encapsulated agent. However, after almost 5h of reaction under T3, there was no microcapsules present in

the solution. Thus, microcapsules were synthesized with only 50%, in mass, of diethylene glycol as encapsulated compound.

From the FTIR spectra, presented in appendix B, Fig.B 10, it is possible to observe that the O-H band has a lower intensity, when compared to the one obtained for the microcapsules with glycerol and diethylene glycol. Since the DEG molecule has two O-H groups it was expected that the intensity of this band was higher. This result may indicate a less amount of encapsulated compound.

Regarding the leaching test results, presented in Fig.C 10, appendix C, it was observed that, for these microcapsules, the viscosity values of the Ongronat® 2500 are low, even after 240h. The obtained results are identical to the ones obtained with 10T:0M:10G.

The foam tests results, presented in Table 42 and Table 43, show that these microcapsules neither contributed to the curing time test nor to the string, tack and cutting time test results.

Table 42- String, tack and cutting time results with the 10T:0M:10G microcapsules with glycerol and DEG, and the respective references

Synthesis	String Time	Tack free Time	Cutting Time
	Seconds	Minutes	Minutes
Reference	45	19	97
Microcapsules with DEG	40	15	77
Reference of 10T:0M:10G	120	39	150
10T:0M:10G microcapsules	60	24	90

Table 43 – Curing time results with 10T:0M:10G microcapsules with glycerol and DEG, and the respective references

Synthesis	Curing Rate at 10%RH			
	24h	48h	67h	72h
Reference	-1	1	-	4
Microcapsules with DEG	-2	0	-	3
Reference of 10T:0M:10G	-4	-3	-2	-
10T:0M:10G microcapsules	-3	-1	-1	-

Conclusions:

It was possible to successfully synthesize microcapsules with glycerol carbonate as encapsulated compound as well as microcapsules with DEG and glycerol.

The microcapsules with glycerol carbonate seem to have more amount of encapsulated compound than the ones with DEG and glycerol.

The microcapsules with only glycerol seem to be the ones that have a more significant effect in the curing of the foams.

4.2.5. "Pre-scale-up"

To finalize the Greenseal Research internship, a pre-scale-up study of a previously selected synthesis was made. In this study, two major alterations were made: the amount of the reactional reagents was doubled, and a heating mantle was used. Thereby, besides the pre-scale-up, the reactional conditions were also adjusted due to the use of the mantle.

For this study to succeed, some alterations were needed in the following reactional parameters: agitation velocity of the emulsion formation; reactional times and amount of aminosilane used in the synthesis.

The microcapsules chosen for this pre-scale-up study were 20T:0M:0G:10A. This choice was made taking into account that more studies are needed in order to obtain hybrid microcapsules, with desirable characteristics using MTES or GPTMS. Thus, silica based microcapsules were chosen. However due to the high leaching observed in these capsules, the study was made with the amino-functional silica second shell ones.

The "reference" in this study are 20T:0M:0G:10A, previous to the pre-scale-up.

- **Agitation velocity of the emulsion formation:**

With the increase of the amount of the reagents and, consequently, the volume of the emulsion solution, the velocity applied with the Ultra-turrax was increased. In order to obtain emulsions with approximately the same dimensions as the ones obtained previously to the pre-scale-up, several velocities were experimented. Initially an initial velocity was chosen, 9200rpm, however the emulsions obtained were of big dimensions. Several attempts were made, until the optimal velocity for the emulsion formation was determined, being 9800rpm. The emulsions obtained with the referred velocity are presented in Fig. 58.

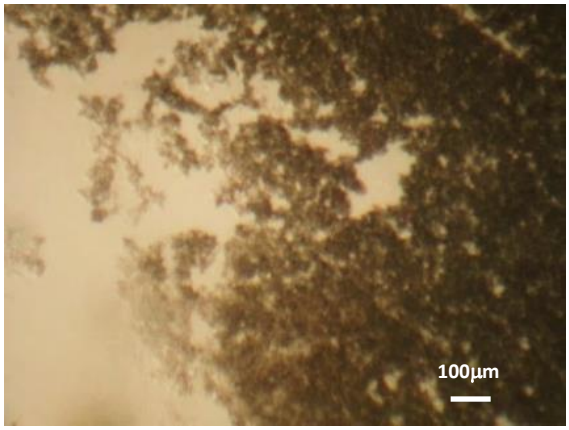


Fig. 58- Emulsion obtained with 9800rpm with the ultra-turrax, under optical microscope

- **Aminosilane**

Since the aminosilane is also a reactional catalyzer, it was important to study the period of time needed for it to react. If it was left for a long period of time, matrix microcapsules were obtained instead of poly-nucleated ones. Thereby, after the addition of the silane to the reaction medium, a sample was continuously collected, filtrated and observed under optical microscope, in order to understand the degree of poly-condensation reaction. The reactional time that led to better results was 6 minutes.

- **Temperatures applied and reactional times**

With the new heating mantle, the temperature increase was much faster with the than it was with the oil bath. Thus, a gradual increase of the temperature was opted, with more temperature steps, each one with short duration.

Fig. 59 presents the following of the pre-scale-up synthesis after optimization

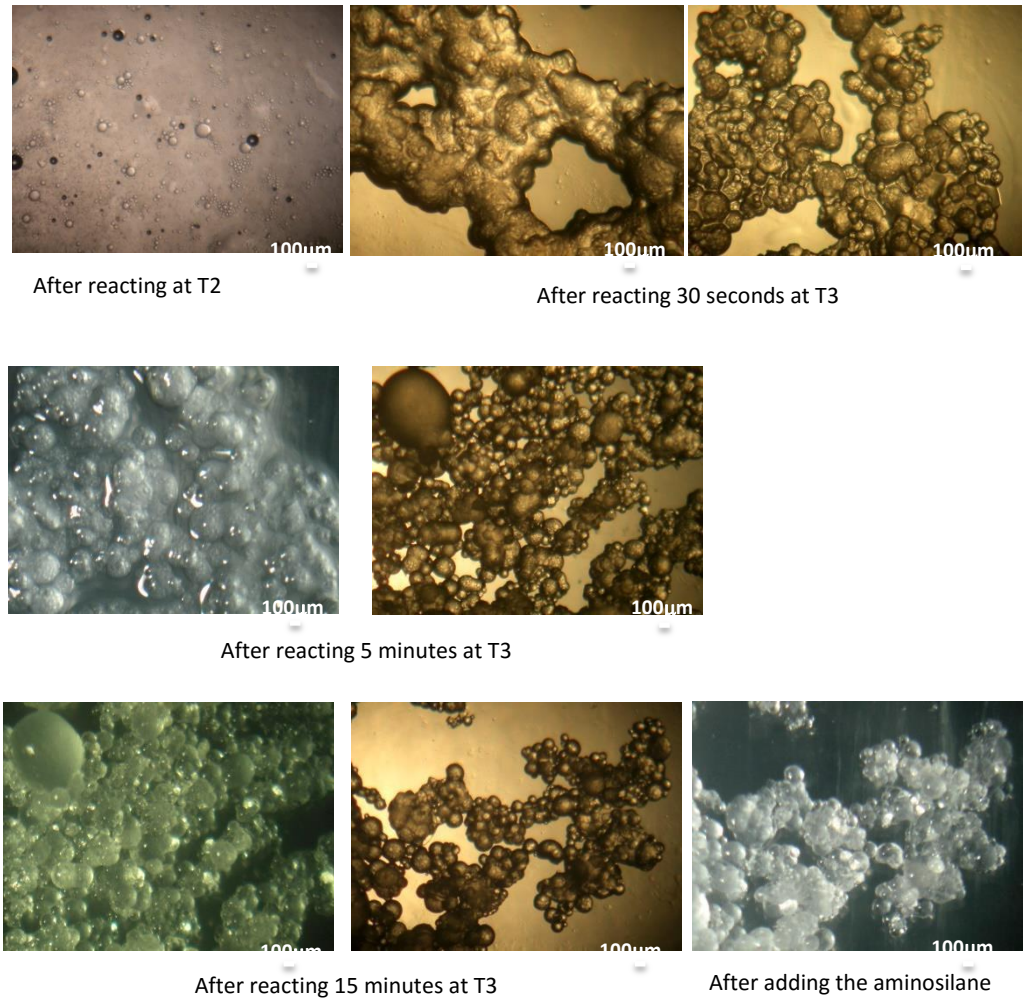


Fig. 59 - Following of the pre-scale-up synthesis after the optimization

Experimental results:

In Fig. 60 it is possible to observe that the obtained microcapsules have an almost perfect spherical shape and are loose, not aggregated, microcapsules. In Fig. 61 it is possible to conclude that these microcapsules are poly-nucleated, as it was desired. More than one reproduction of this synthesis was made and the microcapsules obtained were always poly-nucleated. It was also possible to conclude that the microcapsules' size vary between 50μm and almost 300μm. In comparison, the reference microcapsules had a smaller sizer distribution, between 50μm and 200μm, however the microcapsules were more aggregated.

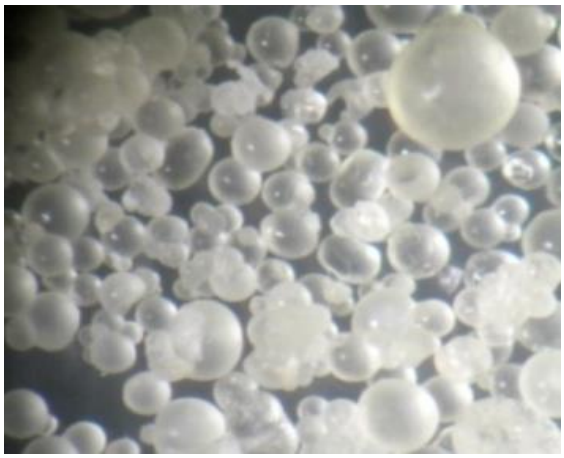


Fig. 60 pre-scale-up microcapsules observed under optical microscope

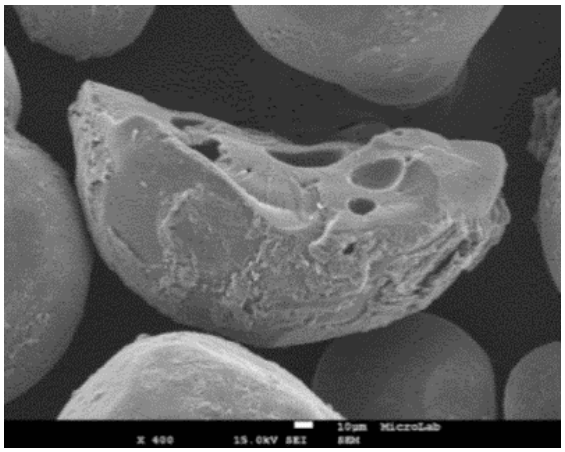


Fig. 61– SEM of pre-scale-up microcapsules, with 400x magnification

From the FTIR results, presented in appendix B, Fig.B 11, it was observed that the microcapsules obtained through the pre-scale-up synthesis have a less intense O-H band when comparing with the silica based microcapsules, with a decrease of around 5%. Also, comparing the TGA results obtained with these microcapsules, presented in Table 44, with the respective thermogram presented in appendix D, Fig.D 8, and the TGA results obtained with the reference ones, is possible to conclude that there was a decrease of the percentage of the microcapsules' weight corresponding to encapsulated glycerol. In the pre-scale-up microcapsules, the glycerol is 21,52% of the microcapsules weight, in the case of the reference capsules, is 24,25% of the total weight.

Table 44 –TGA results obtained with the microcapsules synthetized through the pre-scale-up synthesis

Onset Temperature,°C	Average Temperature,°C	% of mass lost until 300°C	% of water
147,44	218,3	21,52	≈0

Regarding the leaching test results, presented in Fig.C 11, appendix C, it can be seen that there was observed almost no leaching with these capsules, as it was observed with the reference ones. When comparing with the silica based microcapsules, a significant decrease can be noticed with the ones obtained in the pre-scale-up synthesis.

Regarding the synthesis yield, the pre-scale-up synthesis had an yield of 55,10%, which is similar to the one obtained for the silica based microcapsules (57,7%). However, it showed a decrease when comparing with results obtained for the reference, that had a yield of 66,4%, a difference superior to 10%.

The foam tests results are presented in the Table 45 and Table 46. As it can be seen, the microcapsules obtained in the pre-scale-up synthesis did not lead to a significant result for both tests. However, when using a nozzle, it was possible to observe a decrease of 30 minutes in the cutting time results with these microcapsules, which represents an improvement of 44% when comparing with the reference foam. This result may indicate that the microcapsules are not breaking during the spray process, without the use of the nozzle. The results obtained with the reference microcapsules showed that the foam tests results were also not very significant without the use of a nozzle.

Table 45 String, tack-free and cutting time results for the pre-scale-up microcapsules and 20T:0M:0G:10A, as well as the respective references. Not all the synthesis were sprayed in the same day. Therefore, there are two different references. The reference (1) corresponds to the synthesis (1). The same is applied to reference (2)

Synthesis	String Time	Tack free Time	Cutting Time
	Seconds	Minutes	Minutes
Reference (1)	105	11	75
Pre-scale-up synthesis (1)	90	11	67
Pre-scale-up synthesis with nozzle 12 (1)	89	11	42
Reference (2)	88	31	118
20T:0M:0G:10A microcapsules (2)	80	20	-
20T:0M:0G:10A microcapsules with nozzle 12 (2)	31	24	70

Table 46 - Curing time results for the pre-scale-up microcapsules and silica based with second amino-functional silica shell, as well as for the respective references

Synthesis	Curing Rate at 10%RH			
	0h	24h	48h	72h
Reference	-4	-3	-3	1
Pre-scale-up synthesis	-4	-4	-4	-2
Reference	-5	-4	-3	-
20T:0M:0G:10A	-5	-3	-2	-

Conclusions:

It was possible to successfully obtain silica based microcapsules with a second amino-functional silica shell through a pre-scale-up synthesis.

The obtained microcapsules were poly-nucleated, as desired, had a perfectly spherical shape and were not aggregated.

The obtained microcapsules seem to have almost no leaching and the results in the foams were identical to the ones obtained before the pre-scale-up, although the yield was a little lower.

4.2.6. Comparison between microcapsules and microspheres

In this chapter a brief comparison between the results obtained with shell and matrix shell microcapsules will be made, for the case of 20T:0M:0G microcapsules.

Both matrix and core shell microcapsules ones were obtained using two surfactants.

From FTIR results, presented in appendix B, Fig.B 12, it is possible to observe that the intensity of the O-H band is similar for both synthesis, with a difference of 1,15%. The matrix type microcapsules were the ones with the highest intensity of the O-H. From observation of the SEM results, presented in Fig. 62 it is possible to confirm that most of the core shell microcapsules are broken, which may lead to a significant reduction of the encapsulated glycerol.

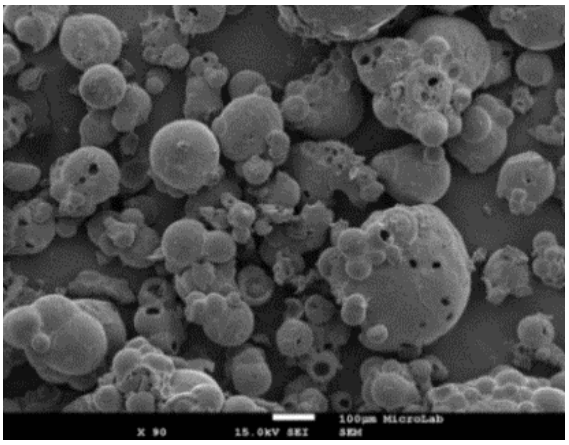


Fig. 62 – SEM results for core shell silica based microcapsules.

The leaching test results are presented in Fig.C 12, appendix C. As it can be seen, the results obtained with core shell and matrix microcapsules were not very different. The Ongronat® 2500 with the matrix microcapsules reached the limit imposed before the core shell ones, but only with a difference of 48h. However, the majority of the core shell microcapsules were broken and they might have already lost much of the encapsulated glycerol. Thus, it is difficult to predict these microcapsules behavior regarding the leaching, since if the microcapsules have not lost the glycerol, the Ogronat2500 could have reached the limit imposed much earlier.

The results obtained in the foam tests, presented in Table 47 indicate that, although the majority of the core shell microcapsules appear to be broken and some glycerol might be lost, they are still the microcapsules that show a more significant result in the curing of the foams. It might be possible because the matrix microcapsules might not be breaking during the spraying process.

Table 47 - Curing time test results for matrix and core Shell silica based microcapsules

Synthesis	Curing Rate at 10%RH			
	0h	24h	48h	72h
Reference matrix shell	-4	-3	-3	1
Matrix shell microcapsules	-4	-3	-3	1
Reference core shell	-5	-4	-3	-
Core shell microcapsules	-4	2	2	-

Conclusions:

The core shell microcapsules appear to have a more significant effect in the curing of the foams, than the matrix ones. However, they might be too fragile, since the majority of the core shell microcapsules appear to be broken, leading to a loss of the encapsulating compound. Another disadvantage of fragile core shell microcapsules is that they can break inside the OCF can while handled.

It would be interesting to try to synthetize core shell microcapsules with a more resistant shell, with an increased thickness, or with a more compact shell.

The addition of other silanes could be studied, for example, the possibility of a different post-treatment or the production of a second shell.

5. Comparison between TGA test results

In this chapter, a brief comparison between the results obtained through TGA analysis will be analyzed, in order to compare the amount of glycerol and remaining water in some of the synthetized microcapsules.

In Fig. 63, all the TGA thermograms that were presented in the previous chapters are compiled. The response of the microcapsules with cork to the temperature increase

seem to be more significant and faster than the rest of the microcapsules analyzed. When analyzing the results presented in the Table 48, it can be seen that, until the 300°C is reached, these microcapsules were the ones that presented the most significant percentage of mass loss. Possibly this results are due to the presence of cork, which is an organic compound that might also be degraded at this temperature range, among the glycerol.

All the microcapsules with amino groups, both with amino-functional silica and EDA, seem to have a similar curve response to temperature increase. When comparing the percentage of mass loss until the 300°C, presented in Table 48, it is possible to observe that for all these microcapsules the percentage goes around between 21 and 26%, which is a relatively small range. It is also possible to observe that the microcapsules obtained in the pre-scale-up synthesis are the ones with less amount of encapsulated glycerol, being the silica/epoxy microcapsules the ones with the highest amount.

From Table 48, it is possible to observe that the microcapsules composed only with the silanes are the ones that have lost a lower percentage of mass with the increase of temperature until the 300°C. Having into account that these microcapsules also seem to have some encapsulated water, the percentage of glycerol in the capsules are about 17,73%, in the case of 10T:0M:10G microcapsules, and 15,87%, for the 5T:5M:10G ones, which is far less than the percentage observed for the remaining capsules.

The apparent absence of water in the microcapsules with cork and superficial amino groups in its composition might be due to the hydrophobicity of the cork presented in the shell. For the microcapsules with superficial amino groups in its composition, this absence might be due to the decrease of silica surface exposed to the air moisture, which prevents an eventual superficial water deposition.

It is possible to conclude that the addition of EDA, aminosilane and cork seems to have led to a diminution of water in the microcapsules and an increase of the encapsulated compound, when comparing with the microcapsules composed only with three silanes.

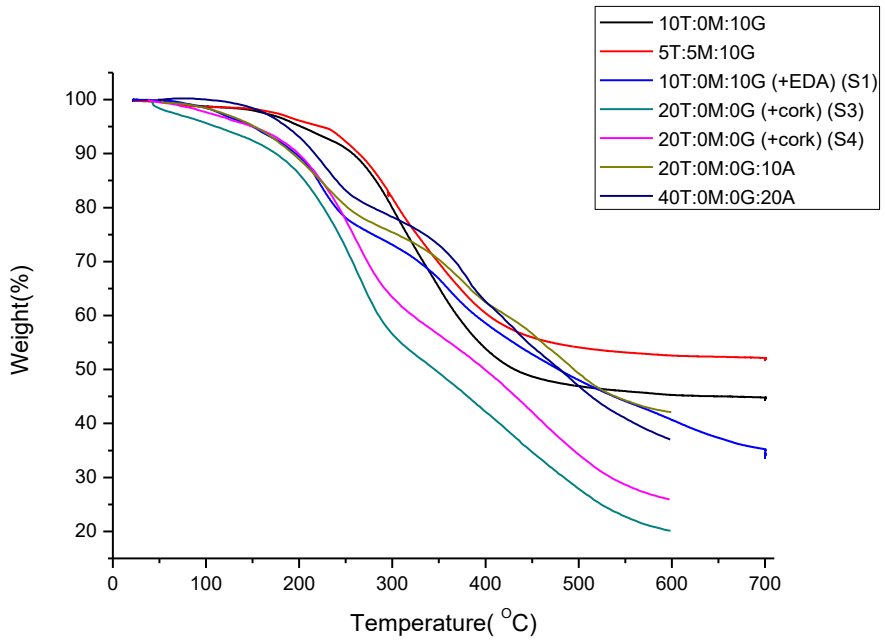


Fig. 63- TGA test results obtained for some of the microcapsules synthetized during this work

Table 48 –Results obtained through the analysis of the TGA graphics, for all the analysis made during this work

Microcapsules	Onset Temperature,°C	Average Temperature,°C	% of mass lost until 300°C	% of water
10T:0M:10G	185,51	257	19,6	1,73
5T:5M:10G	159	259	17,26	1,39
10T:0M:10G (+EDA)	137,29	215,64	26,51	≈ 0
S3	149	216	42,17	≈0
S4	162,94	235,2	35,543	≈0
20T:0M:0G:10A	128	206	24,25	≈0
40T:0M:0G:20A	147,44	218,3	21,52	≈0

6. Waste disposal

Through the microcapsules synthesis in the laboratory, some residues were produced. It was considered that all the silanes added to the synthesis reacted for the microcapsules shell formation and that all the glycerol was encapsulated. Being so, the synthesis reagents that can be considered residues are the decalin and the Span80, used for the emulsion formation, and the hexane used in the filtration step.

The three referred residues were deposited in the same container, which was closed and stored in a ventilated area, away from possible heat and flame sources, before being delivered to the entity responsible for its treatment. It was also necessary to correctly identify the residues' containers to be delivered with the respective LER code, i.e. the European List of Residues. The LER code classifies waste according to its origin and the industrial activity that led to its production. The decalin, the hexane and the SPAN80 can be classified as "Waste organic solvents, refrigerants and propellants", described in chapter 14, with the corresponding code 14 06 03*, "other solvents and solvent mixtures". The chemical compounds that are associated to an LER code with an (*) are considered as hazardous waste pursuant to Directive 91/689/EEC and are subjected to the provisions of that Directive, which aims to ensure ecologically sound of the hazardous waste flow, by setting controls on hazardous waste management.

7. Main conclusions and suggestions of future work

The present work regards the development of microcapsules, containing glycerol, diethylene glycol, or glycerol carbonate in their pores (or core), with the goal of being curing agents for one-component PU foams.

Initially, in this work, the synthesis of inorganic silica based microcapsules was successfully reproduced from previous recipes developed at Greenseal Research. These capsules have a perfect spherical shape, and their presence in the foam seems to contribute to the curing process. However, they also lead to a quick increase of the viscosity of the polyurethane pre-polymer, due to glycerol leaching from the capsules and also residual moisture on their surface, which makes them unacceptable to be used as curing agents. Also, they have relatively big dimensions, which could lead to nozzle obstruction after the first spraying.

Other solutions had to be developed to reach microcapsules of good quality and morphology, which are non-leaching within the pre-polymer inside the pressurized can and which release their content of glycerol upon spraying, leading to a faster curing of the polyurethane foams, independently of the moisture in the air.

Regarding the organically modified (hybrid) microcapsules, the ones with MTES seemed to have a higher performance, when comparing to the ones obtained with GPTMS and the ones with the three silanes. The microcapsules synthesized with 10T:10M:0G were the ones that showed the best results, in terms of morphology and curing speed, which is similar to that obtained for inorganic silica microcapsules, with the advantage that they exhibit a non-leaching performance. The organic functionality of these newly developed microcapsules was responsible for a higher hydrophobicity and, therefore, for a beneficial lower leaching degree. However, the presence of these additional alkoxides (silanes), especially GPTMS, appears to destabilize the emulsion, or affecting the polycondensation reactions, which translates into non-spherical and aggregated microcapsules for some cases and also a lower amount of glycerol encapsulated.

Several reactional parameters were studied, in order to improve the microcapsules' characteristics as well as to decrease its production price. It was possible to obtain microcapsules in all the performed studies, and the majority of the alterations led to improvements in its characteristics. The modifications that led to better results are those related with surfactants, namely the use of two surfactants (one in the dispersed phase and the other in the continuous phase), which promoted the formation of core-shell microcapsules, and the increase of the surfactant amount used in the synthesis, which contributed to the decrease of the microcapsules' size and also the formation of microcapsules with a more spherical shape. Regarding the decrease of the synthesis cost, the most successful change was the usage of an acidic catalyst, which has led to an instantaneous microcapsule formation, contributing to a decrease of the time needed for the reaction to be completed. It would be interesting, as future work, to try to combine the various changes evaluated in this work in the same synthesis, in order to obtain microcapsules with several desired improvements.

Regarding the additional studies performed in this work, it should be referred the addition of EDA to the synthesis with TEOS and GPTMS, which resulted in epoxy resin-rich regions within the silica shell of perfect spherical shape microcapsules, the addition of polydimethylsiloxanes (silicone) to the synthesis with TEOS, which resulted in a silica-silicone shell composition, and the addition of cork powder to the TEOS synthesis, which resulted in a shell of cork-silica composition. All these new approaches led to microcapsules with less glycerol leaching than inorganic silica microcapsules.

Additionally, it was found that the incorporation of aminosilane, at a later stage of the synthesis of inorganic silica microcapsules, acts as a catalyst for polycondensation reaction, leading to the formation of silica based microcapsules with an amino-functional silica (outer) second shell. These capsules proved to be poly-nucleated, with a perfect spherical shape, not aggregated and with almost no leaching, leading as well to an improved curing speed of the polyurethane OCF.

These activities involved basically a comprehensive screening of new compositions for the microcapsules´ shell. Therefore, reproducibility studies and pre-scale-up studies

are required to implement the incorporation of these microcapsules into commercial polyurethane OCF cans.

In the final part of the internship, a pre-scale-up study was made for the silica based microcapsules with an amino-functional silica outer shell. It was possible to establish the successful production at the lab scale of the desired capsules, in batches of ca. 60 g of microcapsules, with a reaction yield of 55,10%.

Besides the good quality of these capsules, it was found that an especially designed nozzle, placed on the aerosol can, helps the burst of the microcapsules and therefore the release of glycerol from the core of the microcapsules to the PU froth, during the spraying process. In this case, a significant result in the curing speed of the PU OCFs is achieved.

So, regarding novelty of this work, a variety of new microcapsules has been developed in the framework of this internship, which, to the best of our knowledge, are not still in the State of the Art, and can be applied in a near future in many varied applications. They include combinations of three different silanes (methyl and epoxy functionality), silica- and epoxy-rich hybrid shells, silica-silicone hybrid shells, cork-silica composite shells, but the best result obtained, in terms of microcapsules spherical morphology, absence of leaching and enhanced curing speed, was for microcapsules composed of silica shell with a double shell of amino-functional silica. This synthesis was successfully scaled-up.

This work has led to plenty of avenues to further explore. It would be interesting to increase the size of the core in the silica-based microcapsules having a second shell of amino-functional silica, in order to encapsulate a higher amount of glycerol, and further improve the curing speed. The encapsulation of an amine based catalyst, in addition to the glycerol, could be also a solution in order to obtain a more significant effect of these microcapsules in the curing process. Also, obtaining microcapsules with slightly bigger dimensions (ca. 300 μm) could be attempted to facilitate their breakage during the spraying process.

8. Work accomplished

Besides developing the present thesis, the experimental work accomplished during the internship in Greenseal Research enabled me the possibility to be author and co-author of the following works:

Presentation poster: Ana C. Marques, Mónica Loureiro, Bruno Sargaço, Luis F. Santos, Auguste Fernandes, Aster De Schrijver, João C. Bordado, “Hybrid microspheres and microcapsules containing a sustainable curing agent for polyurethane one component foams”, Fourth International Conference on Multifunctional, Hybrid and Nanomaterials HYMA2015, Sitges, Spain, 9-13 March 2015.

Article: “Organically-modified silica based microcapsules for high performance curing of polyurethane one component foams”, by Mónica Loureiro, Maria José Lourenço, Luís F. Santos, Aster De Schrijver, João M. Bordado, Ana C. Marques (in preparation).

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Appendix A – Sample acronym table

Table A 1 – Synthesis acronyms and respective silanes' mol percentage

Sample acronym	Silanes in the pre-hydrolyzed solution (mol%)			
	TEOS	MTES	GPTMS	Aminosilane
20T:0M:0G	100	0	0	_
15T:5M:0G	72	28	0	_
10T:10M:0G	46	22	0	_
5T:10M:0G	24	55	21	_
5T:5M:10G	25	30	45	_
15T:0M:5G	77	0	23	_
10T:0M:10G	53	0	47	_
10T:0M:10G (+EDA)	53	O	47	_
10T:10M:0G (+HF)	24	55	21	_
10T:0M:10G (+HF)	53	0	47	_
10T:10M:0G (+ surfactant)	24	55	21	_
20T:0M:0G (2 surfactants)	100	0	0	_
20T:0M:0G (-Hydrolysis)	100	0	0	_
20T:0M:0G (+Glycerol)	100	0	0	_
15T:0M:15G (+EDA)	53	0	47	_
10T:0M:0G (+Baysilone)	100	0	0	_
10T:0M:0G (+Sylopren)	100	0	0	_
20T:0M:0G(+cork)	100	0	0	_
10T:0M:10G(+EDA+cork)	53	0	47	_
20T:0M:0G:10A	68	0	0	32
20T:0M:0G:10A (+Ongronat®2500)	68	0	0	32
10T:5M:0G (+Glycerol carbonate)	72	28	0	_
10T:5M:0G (+Glycerol carbonate)	72	28	0	_
10T:0M:10G (DEG)	53	0	47	_
40T:0M:0G:20A	68	0	0	32

Appendix B – FTIR spectra

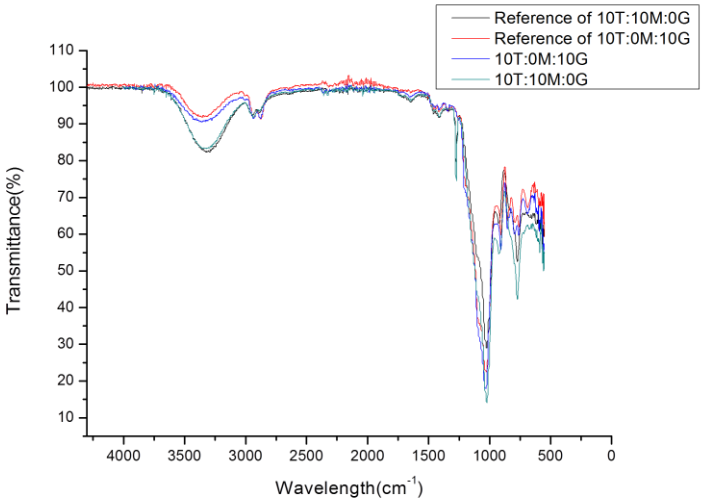

Fig.B 1 - FTIR of the microcapsules obtained with HF

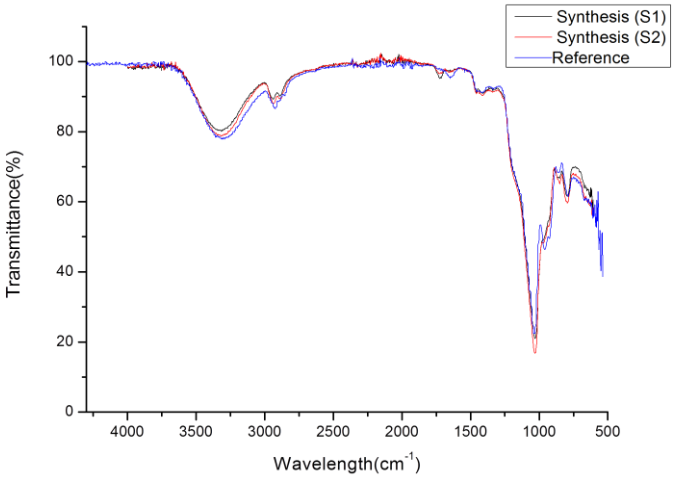

Fig.B 2 - FTIR of the microcapsules obtained with two surfactants

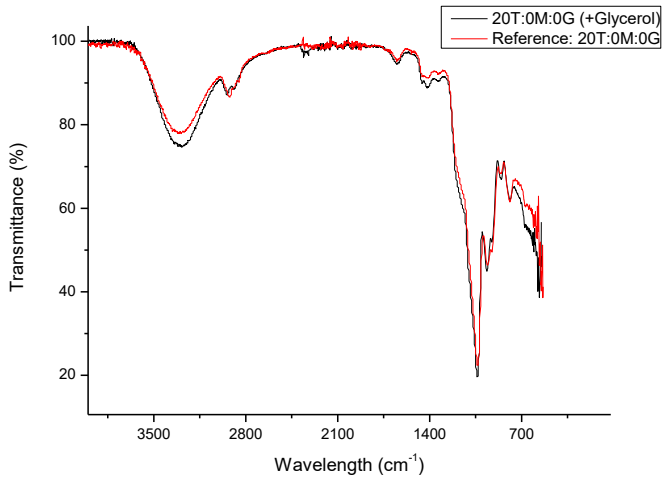

Fig.B 3 - FTIR of the microcapsules synthetizes with more glycerol

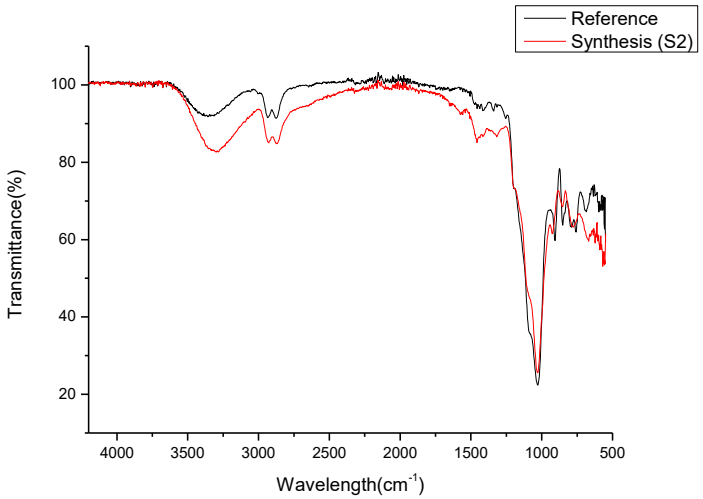

Fig.B 4 - FTIR of the silica/Epoxy microcapsules

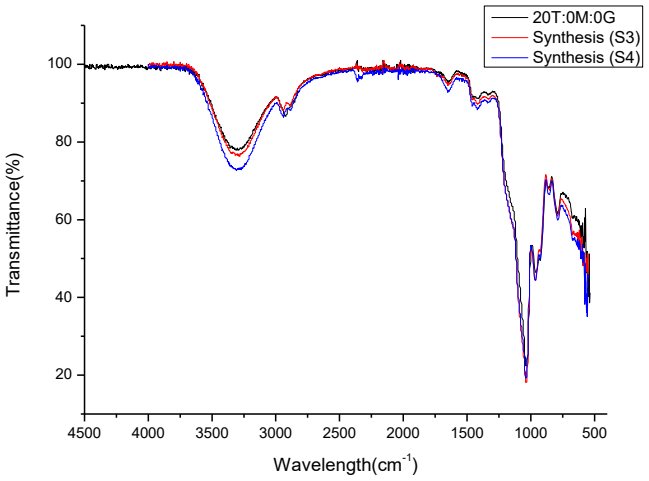

Fig.B 5 - FTIR microcapsules synthetized with Silopren

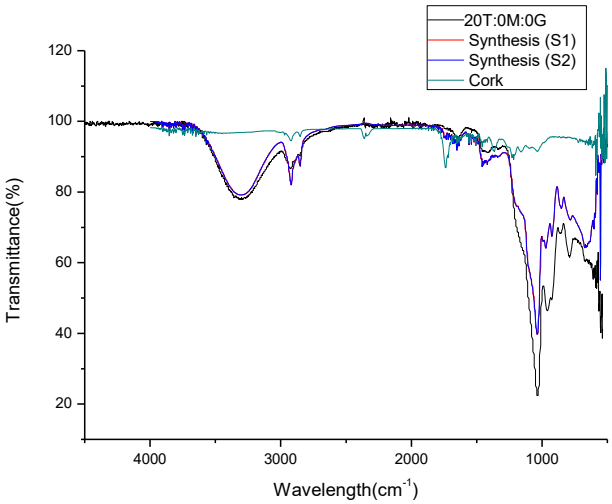

Fig.B 6 - FTIR of the silica based microcapsules with cork

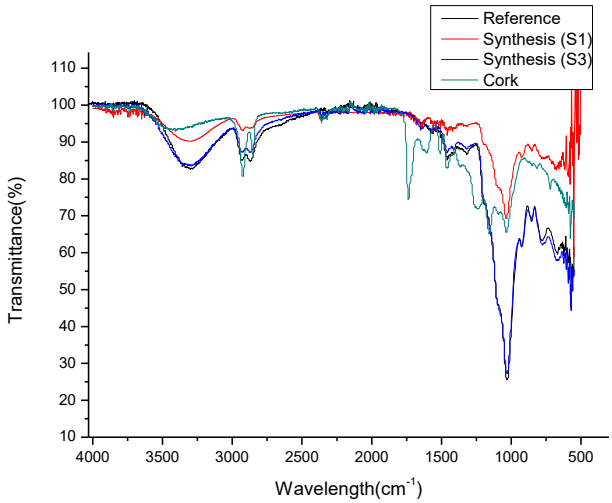

Fig.B 7 - FTIR obtained for the silica/epoxy microcapsules with cork

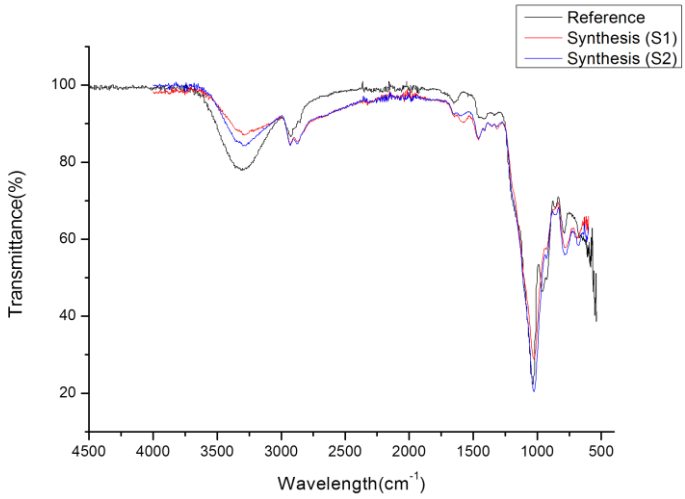

Fig.B 8 - FTIR of silica based microcapsules with an amino-functional silica double shell, synthetized with two surfactants

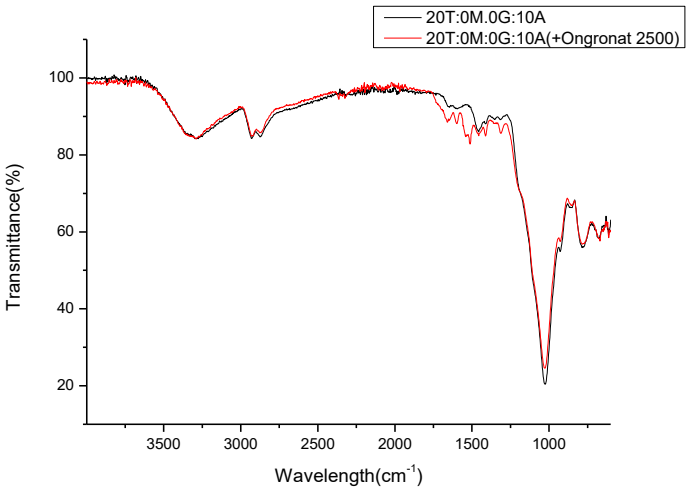

Fig.B 9 - FTIR of microcapsules with Ongronat®2500 post-treatment

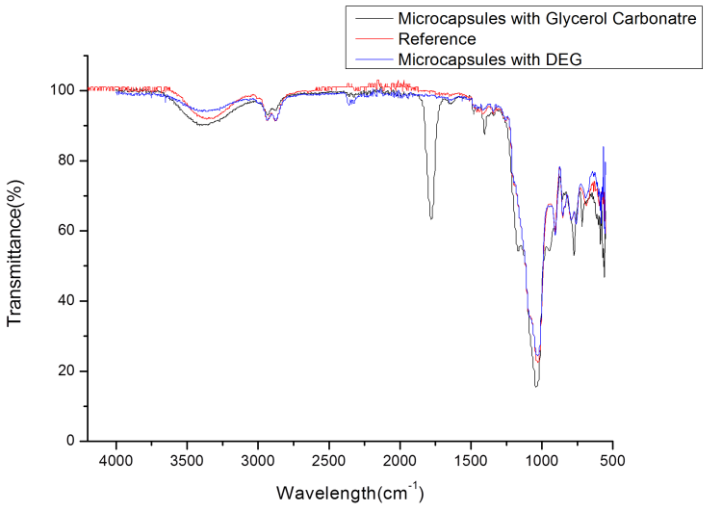

Fig.B 10 - FTIR of microcapsules with DEG and Glycerol Carbonate

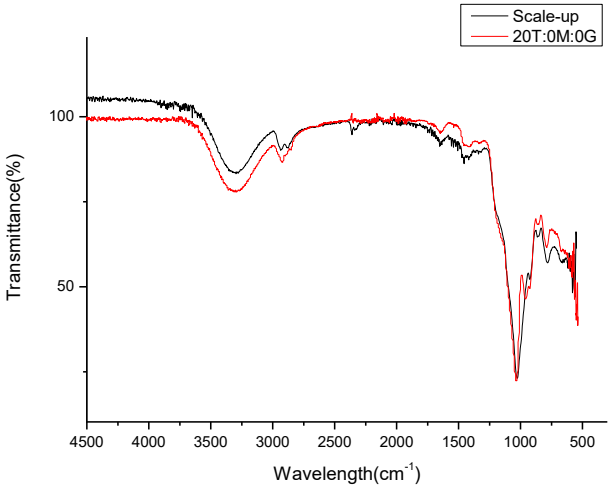

Fig.B 11 - FTIR of microcapsules obtained through the pre-scale-up synthesis

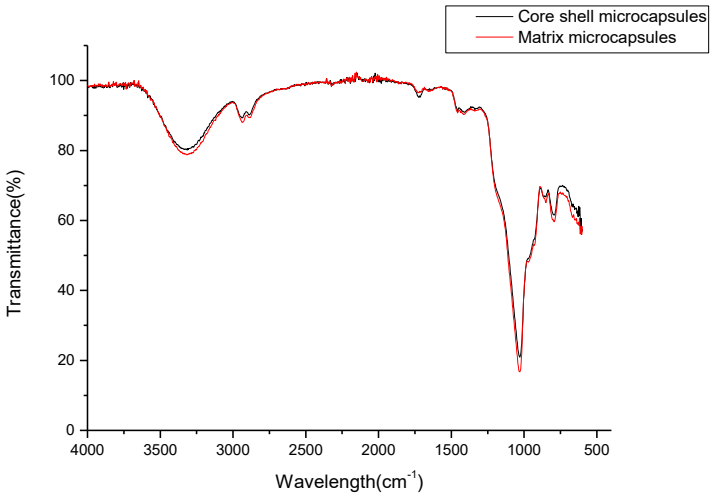

Fig.B 12 - FTIR of core shell and matrix microcapsules

Appendix C – Viscosity Tests

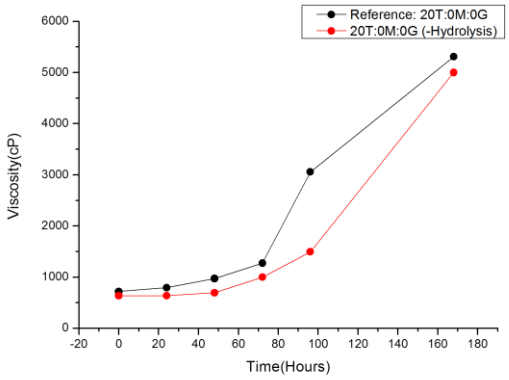

Fig.C 1 - Viscosuty test results for microcapsules synthetized without the pre-hydrolysis step

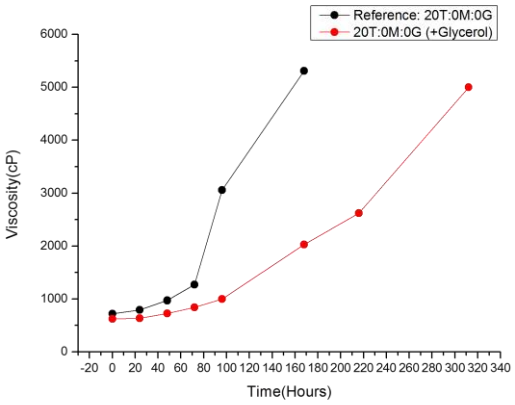

Fig.C 2 - Viscosity test results for microcapsules synthetized with more amount of glycerol

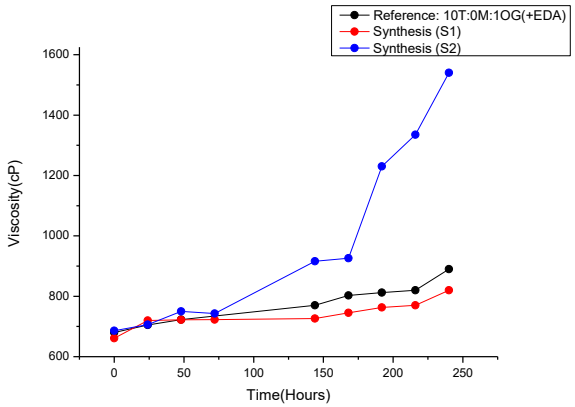

Fig.C 3 - Viscosity results for silica/epoxy microcapsules

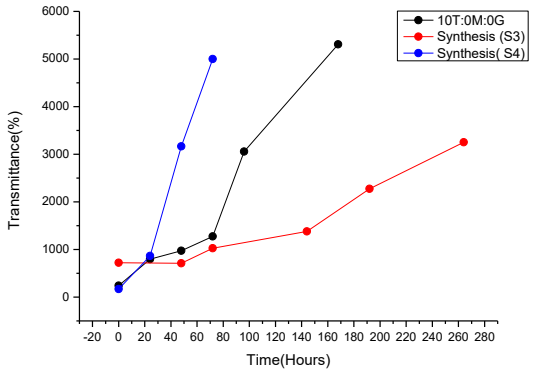

Fig.C 4 - Viscosity test results for silica based microcapsules with Silopren

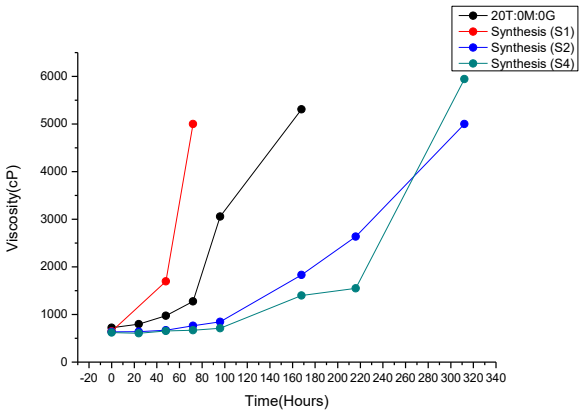

Fig.C 5 - Viscosity test results for silica based microcapsules with cork

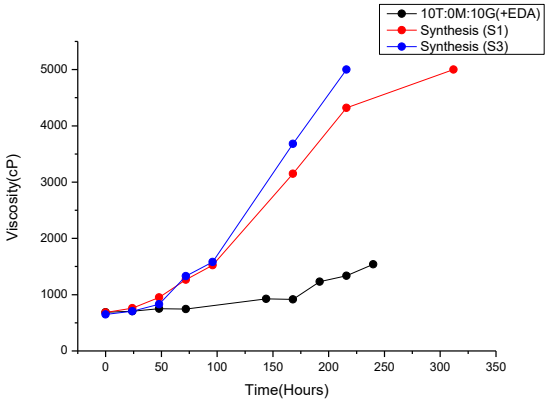

Fig.C 6 - Viscosity test results for silica/Epoxy microcapsules with cork

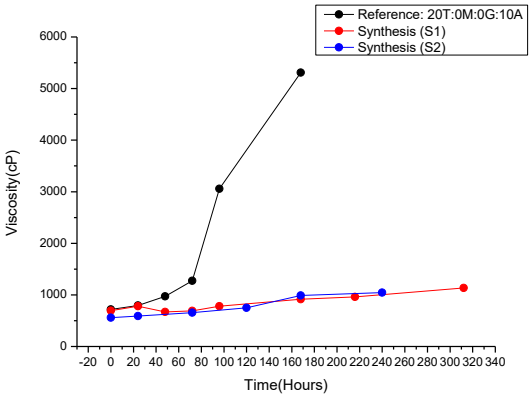

Fig.C 7 - Viscosity test results for silica based microcapsules with an amino-functional silica double shell, synthetized with two surfactants

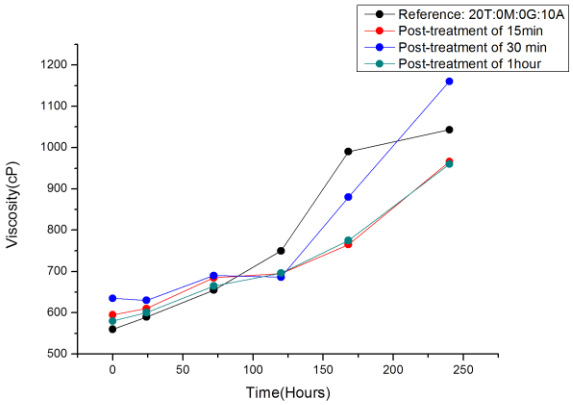

Fig.C 8 - Viscosity test results for Ongronat post-treatment microcapsules

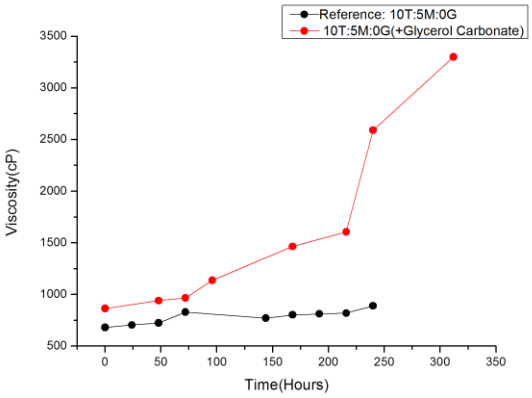

Fig.C 9 - Viscosity test results for the microcapsules synthetized with glyceerol carbonate

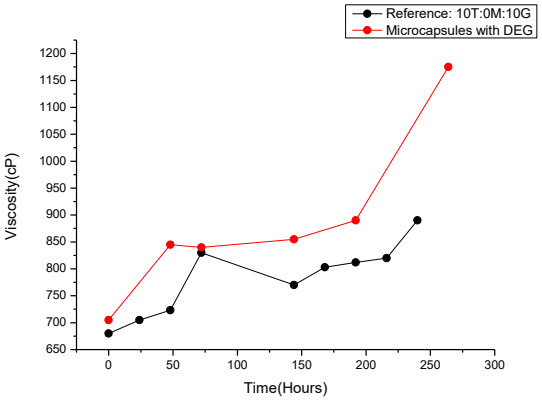

Fig.C 10 - Viscosity test results for microcapsules synthetized with DEG

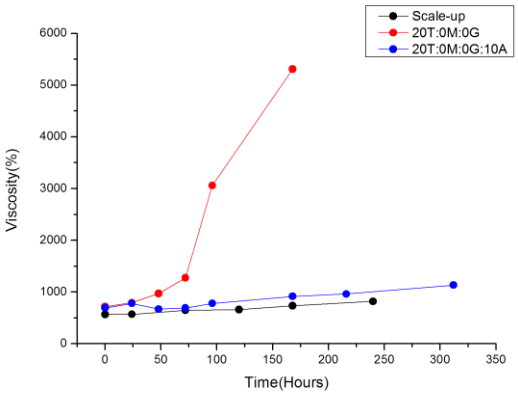

Fig.C 11 - Viscosity test results for microcapsules synthetized through the pre-scale-Up

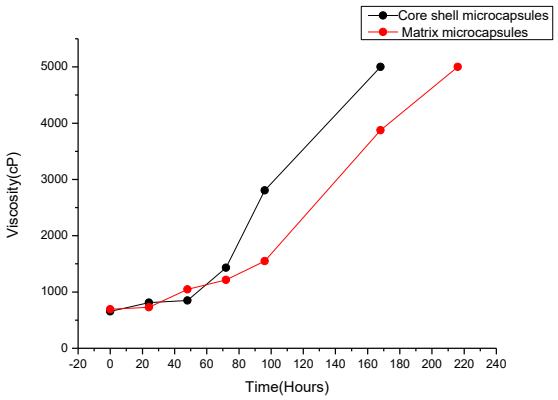

Fig.C 12- Viscosity test results for core shell and matrix silica based microcapsules, synthetized with two surfactants

Appendix D – TGA SThermograms

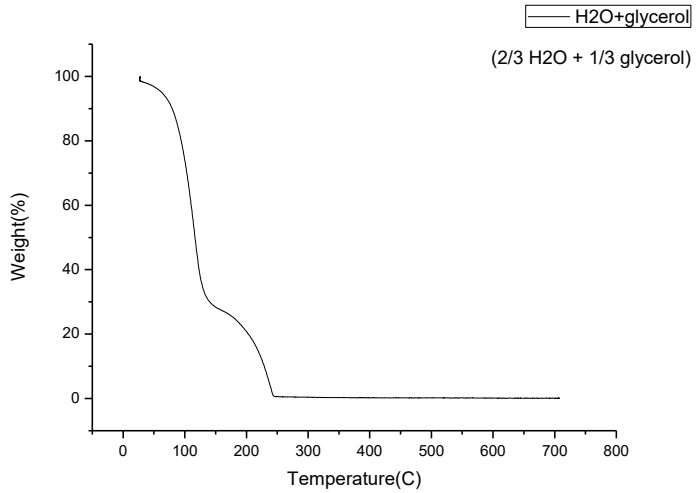

Fig.D 1 – TGA test results for a solution of glycerol in water. The solution was made in the same water to glycerol weight proportions as the solution used for the emulsion formation

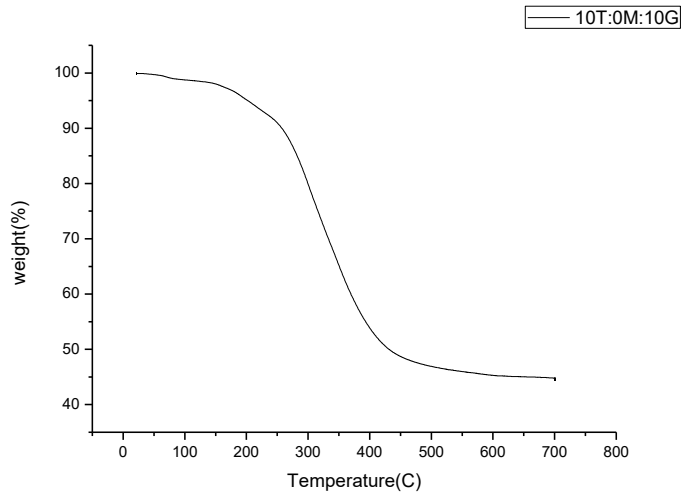

Fig.D 2 – TGA test result for microcapsules synthetized with 10T:0M:10G

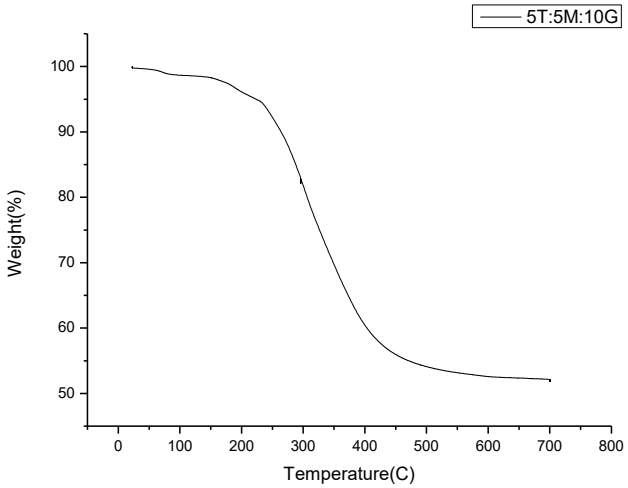

Fig.D 3 – TGA test result for microcapsules synthetized with three precursors, TEOS, MTES and GPTMS.

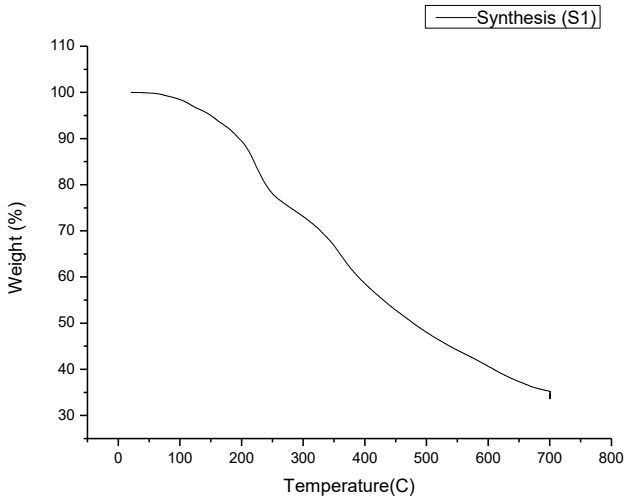

Fig.D 4 - TGA test results for silica/epoxy microcapsules

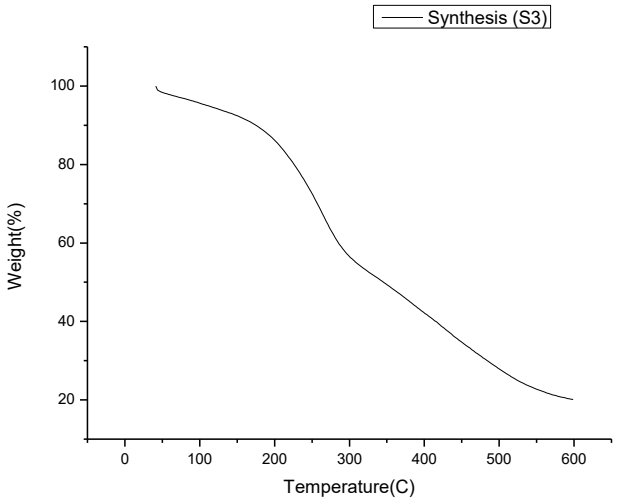

Fig.D 5 – TGA test results of the sílica based microcapsules with cork, synthesis (S3)

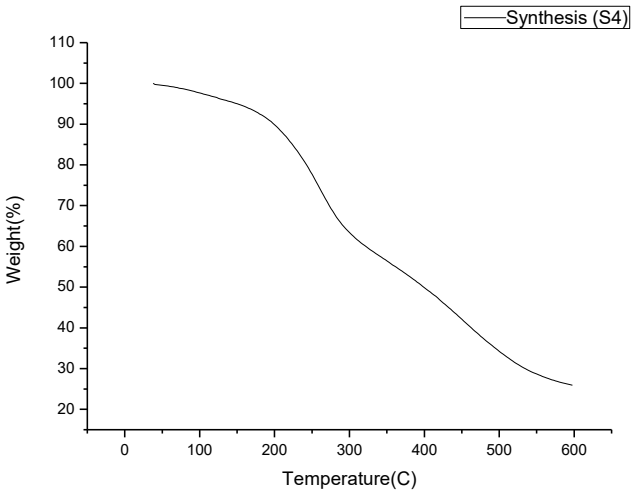

Fig.D 6- TGA test results of the sílica based microcapsules with cork, synthesis (S4)

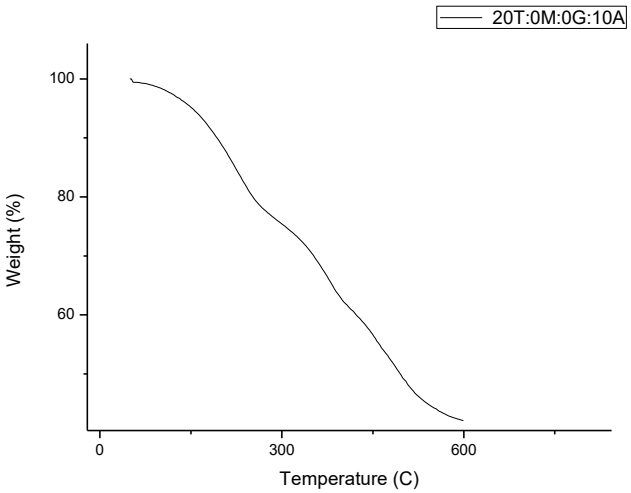

Fig.D 7 – TGA test result of the sílica based microcapsules with a double amino-functional silica shell, with acidified water in the emulsion

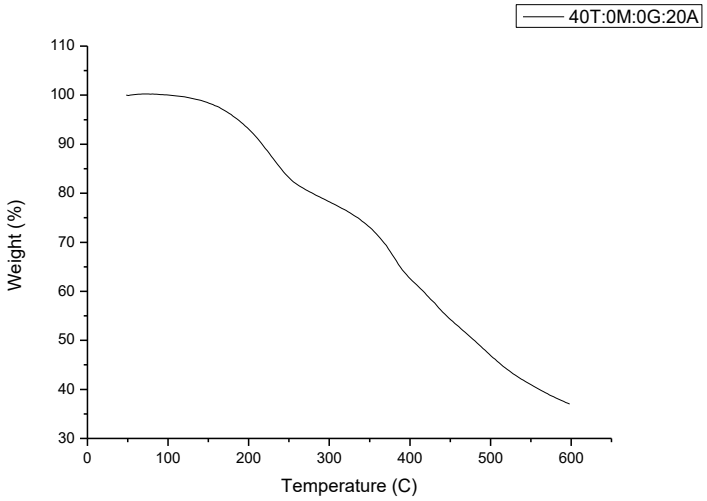

Fig.D 8 –TGA test resulto of the microcapsules synthetized through the scale-up synthesis